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RAPID METHODS

FOR THE

CHEMICAL ANALYSIS

OF

SPECIAL STEELS, STEEL–MAKING ALLOYS, AND GRAPHITE.

BY

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FIRST THOUSAND.

PREFACE.

In offering this little volume the author desires to call attention to the portions of it that he has worked out in his own way and that are, as far as he is aware, new features. (1) A qualitative test for titanium in the *presence* of *vanadium*. (2) The annealed test for chromium in steel. (3) The test for annealing in steel. (4) The pouring of the indicator into the solution when titrating for vanadium and chromium in steel, in the presence of either or both elements. (5) The determination of small amounts of copper and nickel in steel and ferro-vanadium by first separating the copper and nickel from the bulk of the iron and vanadium by means of potassium ferricyanide. (6) The EXACT determination of phosphorus in ferro-vanadium, demonstrating that as little as one-eighth of the actual phosphorus may be obtained by the ordinary processes. (7) The application of the new heating wire to a combustion tube. (8) The modified method for higher per cents of nickel. (9) The determination of silicon carbide in old plumbago crucibles and ITS EXISTENCE THEREIN. (10) The automatic laboratory still. (11) The simple laboratory method for making clay combustion boats. (12) The method for annealing Hadfield's steel. (13) The author's method for the rapid volumetric determination of manganese in the presence of iron, calcium and magnesium, by means of potassium-ferricyanide. (14) The new form of potash absorption and weighing apparatus for carbon dioxide. (15) The new form of combustion train.

The test for annealing in steel was first suggested to

the writer about ten or twelve years ago by Dr. E. S. Johnson. The author has since studied it in its application to all kinds of alloy steels.

It is the author's hope that, at least, some of the information contained in this book may prove as helpful to its readers as it has to him.

PITTSBURG, PA., July 1, 1908.

LIST OF PAPERS.

ANALYSIS OF SPECIAL STEELS, STEEL–MAKING ALLOYS, AND GRAPHITE.

CHAPTER I.

QUALITATIVE TESTS FOR CHROMIUM, TUNGSTEN, NICKEL, AND MOLYBDENUM.

DISSOLVE 0.200 gram of the sample with 5 c.c. 1 : 3 sulphuric acid in 152.4 (6 inches) by 16 mm. test tube. Also 0.200 gram of a plain carbon steel in the same way. Place the two tests in boiling water for a half hour.

The plain carbon steel will be free from black sediment and practically water white as to color. If the unknown contains as little as 0.2 or 0.3 per cent of chromium it will look distinctly greener than the known steel. Nickel also produces this effect, but the color is not so marked.

If the steel has 0.100 to 0.3 per cent of tungsten a black insoluble residue will be found in the bottom of the tube. This black sediment forms also with similar amounts of molybdenum and phosphorus. But on addition of 1 c.c. of 1.20 nitric acid to such a solution the black entirely disappears if due to the presence of the two last named elements. The black precipitate, if caused by a small quantity of tungsten, on addition of the nitric acid, changes to a yellow one. If the amount of the latter is small it is better to put the test tube back on the water bath and permit the tungstic acid to settle for two hours, when it can be seen plainly as a yellow spiral thread rising

up through the solution by giving the test tube a rotary motion. The black residue of phosphide can be recognized by filtering it out and dropping 1 : 1 hydrochloric acid on it, when the characteristic odor of phosphine is obtained. Or it can be dissolved off the filter with 1.20 nitric acid and the filtrate precipitated with molybdate solution after boiling it with a slight excess of potassium permanganate. Finish as in plain steel to get the yellow precipitate. If steels are quite high in silicon, the silicic acid and the carbon, together, produce black flakes that float about. They turn to white ones on being heated with 1.20 nitric acid on a water bath for an hour or two.

The annealed test for chromium is given under "Annealing of Steel." See page 202.

MOLYBDENUM.

A further qualitative test for the latter element is as follows: Dissolve 0.500 gram of sample in 25 c.c. of 1 : 1 hydrochloric acid. Boil till action ceases, using a 254 by 25.4 mm. (10 by 1 inch) tube. Heat further with 2.5 grams of potassium chlorate until a clear solution has been obtained or the residue, if any, is a bright yellow. Add an equal volume of water. Filter without washing. Dissolve 10 grams of potassium hydroxide in 10 c.c. of water. Add this to the filtered solution. Boil for five minutes. Filter. Do not wash. Pour 8 c.c. of this filtrate into a 254 by 25.4 mm. tube. Add conc. hydrochloric acid until crystals form. Dilute with water to 30 c.c. Add a few grains of granulated tin. Heat to the *first* indication of boiling; remove from heat immediately and cool. Add to the cold solution. 2 c.c. of potassium sulphocyanate. A light brownish red indicates 0.2 or 0.3 per cent of molybdenum. A distinct red indicates 1 to 2 per cent and a deep red higher amounts of molybdenum. This is a fine test,

but if the mistake is made of boiling the solution too long with the tin scarcely any color is obtained.   Bring, therefore, to incipient boiling, only, after putting in the grains of tin.   Then remove at once from the fire and test with the KCNS as already described.   For *nickel* the quantitative analysis as given on page 104 is so rapidly carried out that it constitutes an easy qualitative test also.

For qualitative tests for titanium and vanadium see page 5.   For qualitative test for copper in steel see page 92.   For qualitative test for copper in ferro-vanadium see page 13.   For qualitative test for nickel in steel see, also, page 11.

CHAPTER II.

* ANALYSIS OF VANADIUM STEEL AND FERRO-VANADIUM.

THE determination of vanadium in the presence of tungsten, titanium, chromium, nickel, manganese, silicon, molybdenum, copper and aluminum has been studied by the author. It has been the latter's aim to produce modified methods that combine speed, simplicity and accuracy. The underlying reactions are well known and have been variously applied by different chemists.

QUALITATIVE TESTS:

Absence of Titanium.

A qualitative test for vanadium can be completed in a half hour or less, even in the presence of 4 per cent of chromium, although there be but 0.05 per cent of vanadium in solution. Dissolve 0.500 gram of steel in a 254 by 25.4 mm. test tube (10 by 1 inch) in 10 c.c. 1 : 3 sulphuric acid, heating until action ceases, adding a little water, if necessary, to dissolve any sulphate of iron that may separate during the boiling. 5 c.c. of concentrated nitric acid are used to oxidize the iron and hypovanadic acid. Heating is continued until red fumes disappear. If tungsten be present, filter through paper. Filter without washing. Pour some of the filtered or unfiltered fluid, as the case may be, into two 152 by 16 mm. test tubes, allowing about 5 c.c. of the solution to each tube. To one of these portions

* From a paper read before the Pittsburg section of the American Chemical Soc., Jan. 23, 1908.

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add 5 c.c. of sodium peroxide dissolved in dilute sulphuric acid. To the other add 5 c.c. of water. The portion to which the sodium peroxide was added assumes a reddish brown shade if vanadium is present.

If there be enough chromium to give the solution a dark green tint, then hold the tubes against an illuminated white shade. The vanadic solution containing peroxide will plainly show a browner tint than its mate, to which no peroxide was added. The white shade greatly lessens the interference of the chrome green. The peroxide is prepared by dissolving 3.5 grams of sodium peroxide in 125 c.c. of 1.3 sulphuric acid and diluting with distilled water to 500 c.c. Add the water last, when preparing the peroxide solution.

QUALITATIVE TEST FOR VANADIUM IN THE PRESENCE OF TITANIUM.

Recent works on steel analysis give the peroxide qualitative test for vanadium and titanium but dismiss the subject with comment that either element interferes with the qualitative test for the other. The writer has overcome this interference by the use of ferrous ammonium sulphate which, as far as he is aware, is a new departure. By this means as little as 0.100 per cent of titanium can be detected without the least difficulty in the presence of ten times as much vanadium, in spite of the fact that the color of vanadium with peroxide is much stronger than that of titanium and hydrogen peroxide. The principle involved is, briefly, that ferrous ammonium sulphate discharges the brick red color obtained by mixing a vanadic solution with hydrogen peroxide more quickly than it does the yellow shade of the titanic acid and H_2O_2. An extract from the author's experimental records illustrates the procedure. The regular ferrous ammonium sulphate standard as given for vanadium titrations, later

in this chapter, was used for the experiments (A) and (B) and other similar ones.

EXPERIMENT A.

	Reagent.	Result.
Mixture No. 1. {500 mg. plain carbon steel, 8 mg. 8% Ferro Ti, 10 mg. of 21.8% Ferro V, or 0.13% Ti and 0.436% V.	1st, added 5 c.c.H_2O_2 solution. 2d, added 5 c.c. ferrous sulphate. 3d, added 5 c.c. more of sulphate. 4th, added 5 c.c. of H_2O_2 again.	Brick red color. Faded to distinct yellow. Decolorized. Return of distinct yellow.
Mixture No. 2. {500 mg. plain carbon steel, 10 mg. of 22.0% Ferro V, or 0.44% V. No Ti added.	1st, same as above.. 2d, as in 2d No. 1... 3d, as in 3d No. 1... 4th, as in 4th No. 1 .	Brick red color. Brick red nearly all gone. Brick red all gone. No return of red color until 10 minutes had elapsed.

Experiment A was repeated with gradual increase of vanadium up to 1 per cent V, keeping the titanium still at 0.13 per cent, with results identical with the above, so that even with ten times as much vanadium the latter was decolorized more quickly, and was slower in regaining color, when peroxide was again added, than the titanium.

A mixture containing 1 per cent V. with 0.500 gm. plain steel behaved in the same manner as given in B. Vanadium gradually regains its red. A glance at the tabulation shows that, if the chemist wishes to detect titanium in the presence of vanadium, he need only resort to the simple expedient of adding slowly, a c.c. at a time, the ferrous ammonium sulphate standard to the qualitative vanadium test. If it gradually fades from a brick red to a bright yellow then titanium is surely present. But if the red or brown tint

fades directly to a nearly colorless condition without show-
ing a clear bright yellow then, at least, not more than a
trace of titanium is present.

EXPERIMENT B.

	Reagent.	Result.
Mixture No. 1. 500 mg. plain steel, 8 mg. 8% Ti Ferro, or 0.13% Ti.	1st, added 5 c.c. H_2O_2	Distinct yellow.
	2d, added 5 c.c. sulphate.	Do.
	3d, added 1 c.c. more of sulphate.	Do.
	4th added 1 c.c. more of sulphate.	Do.
	5th, added 1 c.c. more of sulphate.	Do.
	6th, added 1 c.c. more of sulphate.	Do.
	7th, added 1 c.c. more of sulphate.	Do.
	8th, added 1 c.c. more of sulphate.	Yellow color less distinct.
	9th, added 1 c.c. more of sulphate.	Yellow color fainter.
	10th, added 1 c.c. more of sulphate.	Yellow color fainter.
	11th, added 1 c.c. more of sulphate.	Yellow color all gone
	12th, added 1 c.c. of peroxide.	Yellow color very strong.
Mixture No. 2. 500 mg. plain steel, 10 mg. 22.5% Ferro V, or 0.44% V.	1st, added 5 c.c. H_2O_2	Strong brick red color.
	2d, added 5 c.c. sulphate.	Red color nearly gone.
	3d, added 1 c.c. more sulphate.	Red color all gone.
	4th, same as above in 4th to 12th, No. 1.	Red color all gone.
	12th, same as above in No. 1.	Red color all gone.
	13th, added 1 c.c. more of peroxide.	Slight return of brown.
	14th, added 1 c.c. more of peroxide.	Faint coffee color.

To render the qualitative tests decisive one should proceed exactly as outlined in the table as to amounts of peroxide and sulphate added.   Under the conditions given the tests are very satisfactory.

Further, the color of plain vanadium steel with hydrogen peroxide is different from that obtained in like manner with titanium.   Much vanadium (0.40 per cent) gives a strong brick red.   Small amounts yield a brown.   Titanium color with hydrogen peroxide is always a clear yellow unless vanadium is present.

The quantitative determination of vanadium and chromium in most varieties of vanadium steel can be made in a comparatively simple way.   The writer proceeds as follows: Two grams of steel are heated in a mixture of 30 c.c. of 1 : 3 sulphuric acid and 20 c.c. of water in a 600 c.c. beaker.   When the first action is over, 60 c.c. of 1.20 nitric acid are used to complete the solution and oxidize the iron.   Boiling is continued two minutes longer when 200 c.c. of water are introduced.   From a small pipette a solution of permanganate of potash is delivered, a little at a time, until a slight precipitate of manganese oxide is obtained that does not perceptibly dissolve after twenty minutes boiling.   The beaker is removed from the fire and, after a few moments, is placed in a tray of water.   Its contents are filtered into a heavy suction flask through an asbestos filter using a $1\frac{1}{4}$-inch carbon filter tube, supporting the asbestos on a perforated porcelain plate. (The asbestos is washed in nitro-hydrochloric acid and freed from chlorine test with distilled water before it is used.)   The residue on the asbestos filter is washed fifteen times with a mixture of 20 c.c. of 1 : 3 sulphuric acid diluted with 500 c.c. of water.

The filtrate and washings are returned to the 600 c.c. beaker together with 30 c.c. of dilute sulphuric acid, additional.   The volume is now about 350 c.c. and titra-

tion is begun with a standard of double sulphate of iron and ammonia. The double sulphate standard is dropped in from a 100 c.c. burette until the fluid in the beaker loses all brown tints and assumes a practically colorless shade, in plain vanadium, or in vanadium steels containing less than 1 per cent of chromium. If much chromium is present, i.e., from 2 to 6 per cent, the iron sulphate is added until the chrome green no longer grows darker, and two or three c.c. more to insure an excess. There are two reasons why the sulphate standard should be added at the start. In the first place, though no chromium may have been added to the steel, there is often a little manganic oxide held in solution, or permanganate, which would reduce a portion of the sulphate standard. Again there is never any certainty that small amounts of chromium are not present. The quantity of sulphate standard required in the foregoing reduction should be noted in case the determination of chromium is part of the program. The permanganate of potash standard is next dropped into the solution and, as soon as the pink color begins to disappear slowly, the standard is added three drops at a time, until a very faint pink color is obtained that persists after 30 seconds stirring. Should even as much as five or six per cent of chromium be present a practiced eye can easily detect pink reflections through the chrome green. These pink glints can be seen in the bottom of the beaker and, as one looks down through the mouth of the latter, a rounded bright spot is seen that takes on a pink flush when the permanganate is in excess.

The solution is now ready for the titration of the vanadium, alone: 0.6 c.c. of potassium ferricyanide is poured into the beaker with a convenient dropper, having an etched mark on it to indicate the 0.6 c.c., so that the same quantity of the indicator is always taken. The ferricyanide imparts a brown tint to the iron solution. The

ferrous ammonium sulphate standard is, again, dropped in, a little at a time, until one drop produces a green coloration that is *free* from yellow tints.   The titration is not carried to a blue.   If much chromium is in solution the double sulphate is added until the green fluid begins to darken The number of c.c. of double sulphate standard required in this second titration less the number needed to produce a similar shade in an imitation test, made with a steel that does not contain vanadium, gives the amount of the sulphate standard required to reduce the vanadic acid present. This remainder is multiplied by 2.54 to obtain the number of milligrams of vanadium in the sample.   With each lot of analyses, two tests are made of plain steels to which have been added known weights of standard ferro-vanadium drillings or powder.   If the usual operations recover the vanadium added all of the tests made at the time are accepted. The amount of double sulphate standard required by the blank tests on non-vanadium steels is deducted from all tests before making calculations.   This deduction for plain vanadium or vanadium-chrome steels where the per cent of chromium is not much in excess of three per cent, varies from 0.4 to 0.9 c.c.   This applies to a volume of approximately 350 c.c.   An increased volume produces an increased blank.   A test, in duplicate, for vanadium by the foregoing manipulations can be carried through in an hour and a half in the presence of chromium, nickel, tungsten, or molybdenum.

The presence of much chromium increases the blank somewhat.   With no chromium present the blank is about 0.3 to 0.4 c.c. and, with chromium in the solution to the extent of 3 per cent, it is 0.7 to 0.9 c.c.   With a chromium content of 4 per cent it is 1.0 to 1.2 c.c.   It is always best to make control tests and blank tests, when high chromium and tungsten steels are being analyzed, with mixtures imitating closely the samples submitted for analysis.   It

is very important when dealing with alloy steels, containing large percentages of chromium and tungsten, to digest the drillings until the tungstic acid is a bright yellow before boiling with the excess of permanganate solution. One should, when the tungsten has " cleaned well," add permanganate until, after 20 minutes boiling, sufficient excess of manganese oxide is present to give the separated tungstic acid a chocolate color. Then proceed as usual.

When nickel is present in the steel in quantities ranging from 3 to 5 per cent the same method applies, but it must be borne in mind that, when ferricyanide of this concentration (5 grams in 130 c.c. of water) is used, in a few minutes, nickel ferricyanide separates, hence the titration must be proceeded with immediately.

Molybdenum does not interfere with the titration of vanadium, though the former element be present in large quantities.

The determination of vanadium in ferro-vanadiums of the low silicon type offers no difficulties except that segregation is considerable. It is always advisable to make at least three tests of each sample and average the results. From 0.3 to 0.6 grams are taken and proceeded with exactly as in steels until the titration is to be made when, instead of adding the double sulphate standard first, the completeness of the oxidation of the ferro-vanadium is tested by adding three drops of the permanganate standard. If this gives a suggestion of pink to the solution, the ferricyanide indicator is added and then the ferrous sulphate standard until the light sky blue of the vanadyl salt is darkened *slightly* by the deeper blue caused by the excess of ferrous standard. This end point is very satisfactory but requires a little experience on the part of the analyst. The amount of sulphate standard used is noted and then the permanganate standard is added, *at once*, until a *distinct*

reddish pink color is obtained that does not fade per-
ceptibly after thirty seconds vigorous stirring. This end
point might be described as an old rose shade. Blanks are
run on the same weights of a plain carbon steel in exactly
the same way and deducted from the amount of sulphate
required to produce the blue and from the amount of per-
manganate required to restore a pink color. If less perman-
ganate be used than the sulphate, after correcting the
sulphate reading to the permanganate basis, the presence of
chromium is indicated and a qualitative test for the latter
element can be made in an hour by fusing 0.8 gram of
the ferro-vanadium with 10 grams of sodium carbonate
mixed with two grams of nitrate of potassium. The melt
is dissolved in water. The residue is removed by filtration
in the cold. A yellow tinted filtrate confirms the presence
of chromium. Several tenths of one per cent of chromium
are frequently present.

The amount of double sulphate should not be taken as
a basis of percentage calculations unless it is positively
known that chromium is absent. The sulphate should
be first added as described. This should be immediately
followed by the addition of the permanganate standard as
given and the amount of the latter standard required to
produce the permanent reddish pink should be multiplied
by 2.54 to find the milligrams of vanadium in solution.
For instance in 50 per cent ferro-vanadium it is not practi-
cal to take more than 0.4 grams for analysis. One c.c. of
the double sulphate equals 0.00086 gram of chromium or
only .215 per cent chromium, but it also equals .635 per
cent vanadium, i.e., 0.2 per cent chromium would raise the
vanadium content .6 per cent if not eliminated by calculat-
ing the vanadium from the permanganate used to obtain
the old rose tint. When ferro-vanadium contains much sili-
con, about 4 per cent or more, the borings or powder may
not dissolve completely in sulphuric and nitric acids. The

following modification is necessary: Treat .3 to .6 gram of sample with 60 c.c. 1.20 nitric acid in a No. 5 porcelain evaporating dish.   When heat produces no further action add 1 c.c. or more of hydrofluoric acid which promptly gives a complete solution.   60 c.c. of 1:3 sulphuric acid are poured into the dish, the watch glass is removed and the solution is evaporated to heavy fumes to remove the hydrofluoric acid.   The sulphates are dissolved in water and transferred to a 600 c.c. beaker and the analysis completed as in low silicon ferro-vanadium.

Ferro-vanadiums containing from 0.5 to 6.0 per cent of copper present a slight obstacle.   When the ferricyanide indicator is added copper quickly produces a light yellow cloud of copper ferricyanide that entirely prevents any end point being seen.   In such cases a trial analysis is run and a trial amount of the indicator is added just before filtering off the excess of manganese.   The copper is thus filtered out with the manganese.   The filtrate is proceeded with as usual and, if no further clouding results on adding 0.6 c.c. more of the ferricyanide indicator, the titration is completed.   Should more clouding occur the analysis is repeated and twice as much indicator is added before filtering off the manganese oxide.   More indicator is added to the filtrate and the analysis completed in the regular manner.   Copper can be separated readily with hydrogen sulphide or by means of potassium sulphocyanate and sulphurous acid, but more time is required and nothing gained.   None of the foregoing tests need consume more than two hours except when much silicon is present and resort to hydrofluoric acid is necessary.

As ferro-vanadium samples are, at times, quite variable it is always best to make several tests of the latter and report an average of the results obtained.   If the copper content does not exceed 0.3 to 0.4 per cent, even when two

grams of sample are taken, the vanadium can be titrated before the clouding begins if it is proceeded with as quickly as possible after the addition of the ferricyanide.

Small Amounts of Vanadium.   For the determination of small amounts of vanadium, ranging from 0.02 to 0.05 per cent, it is expedient to dissolve six to eight grams of the steel for analysis.   Such large weights of steel are treated first with 60 c.c. of 1:3 sulphuric acid and 100 c.c. of water.   When this action is over 120 c.c. of 1.20 nitric acid are added to complete the solution and to oxidize the iron.   Then continue the analysis as usual.   Blanks should be carried along with equally large amounts of a plain carbon non-vanadium steel.   The writer would advise against the addition of manganese sulphate to discharge any persistent pink color when boiling with permanganate as its use, in the method as given, seems to increase blanks, apparently causing part of the permanganate to pass into solution in the manganic condition.   Even the blank filtrates have a brown tint as though containing a few hundredths of one per cent of chromium.   This would seem, in a measure, similar to the solution of iron hydrate in iron salts.   On discontinuing the use of the manganese sulphate, lower and more uniform blanks and freedom from brown tints, therein, were attained.

If pink colorations occur due to excessive additions of the permanganate, dilute further with distilled water and a drop or two of ferrous sulphate and boil until they are destroyed.   It is rare that distilled water does not contain enough traces of organic matter to accomplish this purpose. A pink color in the analysis of ferro-vanadium does no harm in the determination of vanadium as the sulphate standard is added at the start; and the vanadium is calculated from the amount of permanganate required to produce an old rose shade, after getting the blue with the sulphate standard and ferricyanide indicator.

CARBON.

The high-carbon, low silicon ferro-vanadiums decarbonize readily in the electric furnace with oxygen only. The lower carbon grades and high silicon varieties yield better if they are mixed with an equal weight of red lead, if burned in the electric furnace, or with four times their weight of red lead in the ten burner Bunsen combustion furnace.

NICKEL.

Large amounts of vanadyl salts in solution yield ammoniacal citrates of a very dark green color, making it an impossibility to see end points in a cyanide and silver titration. The *vanadic* salts are free from this objection: Dissolve one gram of the ferro-vanadium in a mixture of 30 c.c. of 1:3 sulphuric acid and the same quantity of 1.20 nitric acid. Use a little hydrofluoric acid and then evaporate to fumes with sulphuric acid, as already described in this chapter, if there should be an insoluble residue after heating with the mixed acids first mentioned. Boil the sulphuric and nitric solution, or the water solution of the fumed residue, with an excess of permanganate; filter out the oxide of manganese; wash it with sulphuric acid water. Neutralize the free acid in the filtrate with ammonia *before* adding the citric acid or the latter will reduce the vanadic to hypovanadic acid again. Then add a slight excess of ammonia to the clear solution and titrate the nickel in the regular way with cyanide and silver nitrate. (See Chapter IX.) If copper is present it will interfere and the method given in Chapter VIII, part 2, is the simplest way to prevent the interference due to copper, and, also, affords an expeditious plan to obtain the percentage of the latter element in the same analysis.

MANGANESE.

The manganese is obtained as in steels, by dissolving 0.050 to 0.100 gram of sample in 40 c.c. 1.20 nitric acid, boiling off red fumes, further boiling for four minutes with lead peroxide of a light brown color. Very dark brown to black looking lead peroxide should be rejected, as the black looking variety invariably gives low results. In the writer's experience with different lots, the black-brown peroxide gives results from ten to twenty per cent too low. After boiling four minutes with the brown peroxide the solution is promptly put into cool water and from there into cold water. After the excess of lead peroxide has been allowed to settle for ten minutes, or more, if convenient, the pink solution is carefully decanted into a 5 ounce beaker and titrated with a standard solution of sodium arsenite until the pink shade is gone and the slight yellow of the nitrate of iron appears.

Chromium gives high results by the process just described and must first be removed as follows: Dissolve 0.150 or 0.30 gram of the chrome or chrome-vanadium steel in 5 c.c. of 1:3 sulphuric acid in a 250 by 25 mm. test tube, warming gently till action is over. Warm further with 10 c.c. of 1.20 nitric acid and boil off red fumes. Cool to room temperature; dilute to about 30 c.c. with water. Add a rather thick cream of zinc oxide until the ferric and chromic hydrates begin to settle leaving a ring of clear fluid on the top. Cool again and dilute to the 75 c.c. mark. Close the tube with a clean rubber stopper and mix the contents of the test thoroughly by repeated inversions of the tube. After the precipitate has settled somewhat, filter through a dry filter into a dry beaker. Rinse a 25 c.c. pipette 3 times with some of the filtrate and then deliver 25 c.c. into a 250 by 25 mm. test tube, add 15 c.c. of concentrated nitric acid, bring to boil, add lead peroxide, boil four minutes

and finish as in plain steels.   This process can be carried through in forty-five minutes and is entirely accurate for technical analysis to two per cent of manganese.   The author has encountered ferro-vanadium with as much as 5 per cent of manganese together with high silicon.   In such cases a gram of the substance is fused exactly as though aluminum were being sought for.   The water solution of the melt is warmed with alcohol (a few drops) until all green colorations are discharged.   The insoluble residue is filtered out; washed with sodium carbonate water; dissolved off the filter with hot 1:1 hydrochloric acid; evaporated to thick fumes of sulphuric acid in a porcelain dish.   The residue is dissolved with water.   Transferred to a liter flask.   Diluted to 500 c.c.   Precipitated with zinc oxide; diluted to one liter and finished as in high manganese in ferro titanium.   See page 44.

High Silicon and Low Manganese Ferro-vanadium.

Such ferros cannot be analyzed for manganese as in steels on account of partial insolubility in nitric acid.   Dissolve 0.100 gram of the alloy in a small porcelain dish or crucible, as far as possible, with 10 c.c. 1.20 nitric acid.   When action is over, add hydrofluoric acid drop by drop until, with a little further heating it dissolves all to a clear solution and no gritty or metallic particles remain.   Add 20 c.c. 1:3 sulphuric acid and evaporate to thick fumes.   Cool and dissolve the sulphates in 10 c.c., or more, if necessary, of water, heating until clear solution is attained.   Wash into a 10 by 1 inch test tube.   Dilute to 20 c.c. with water.   Add 10 c.c. of conc. nitric acid.   Boil with brown lead peroxide and finish as in steels.   High silicon ferro-vanadium with manganese above 2 per cent could be assayed by taking 1.0 gram of sample.   Heat with 30 c.c. 1.20 nitric.   Clear all insoluble matter with hydrofluoric

acid. Add 60 c.c. 1:3 sulphuric acid. Evaporate to thick fumes. Dissolve in water. Transfer to a liter flask. Dilute to about 500 c.c. with water. Add a slight excess of zinc oxide. Dilute to the liter mark. Mix thoroughly and finish as given for high manganese in ferro-titanium.

Sulphur.

Ferro-vanadium does not dissolve completely in dilute hydrochloric acid so that even approximate sulphur tests by evolution are not available. To determine sulphur in low silicon ferro-vanadium dissolve three grams of sample in one hundred c.c. of concentrated nitric acid in a 600 c.c. beaker. When action ceases add immediately 50 c.c. of concentrated hydrochloric acid for, in alloys containing thirty-five and higher percentages of vanadium, a red precipitate settles out in large quantities if hydrochloric acid is not present to dissolve it. The presence of the red precipitate has a disadvantage. It causes the contents of the different beakers to spurt. Two grams of carbonate of soda are added. The solutions are transferred to No. 6 porcelain dishes and evaporated to dryness. The residue is dissolved in 100 c.c. of hydrochloric acid and evaporated again to dryness. Solution is once more effected with 50 c.c. of conc. hydrochloric acid followed by evaporation to a scum. Ten c.c. of concentrated hydrochloric acid are employed to dissolve the scum; 100 c.c. of water are added; the solution is filtered; diluted to 300 c.c. and the sulphate precipitated with barium chloride, using 60 c.c. of a saturated solution diluted with 240 c.c. of water. Blank determinations are made of exactly the same reagents and the sulphur found is deducted. One gram of highly silicious ferro-vanadiums is fused with a mixture of 20 grams of sodium carbonate and four grams of potassium nitrate. The fusion is dissolved in water, acidulated

with hydrochloric acid, evaporated twice to dryness, taken up with 20 c.c. of concentrated hydrochloric acid and sufficient water to dissolve the sodium chloride, and filtered. The sulphate in the filtrate is precipitated with barium chloride solution.

Aluminum.

Aluminum cannot be separated from vanadic solutions by ammonia. The latter are not precipitated by ammonia alone, but if iron or aluminum be precipitated in the presence of vanadic or vanadyl salts, large quantities of the element are carried out of solution by the iron or aluminum in a manner analogous to the precipitation of phosphoric acid by means of ferric salts and ammonia.

The following procedure gives a highly satisfactory separation. Fuse 0.815 gram of ferro-vanadium in a mixture of 10 grams of sodium carbonate and two grams of potassium nitrate. Raise the heat very gradually. Keep molten for a half hour. Dissolve the melt in water; mix with filter-paper pulp; filter; wash with water containing a little sodium carbonate. Return the washed residue to the crucible in which the fusion was made; roast, and fuse it again with the same mixture. Dissolve the fusion in hot water, preferably in a platinum dish; cool; add paper pulp made from ashless filter paper; filter and wash as before. Combine the two filtrates, heat same almost to boiling, volume being about 400–600 c.c.; remove from flame; add from a burette 1 : 1 hydrochloric acid, i.e., 1.093 specific gravity at 29° C. Hold the cover on the beaker in an inclined position to permit of stirring without loss of spray. Continue the addition of the acid until aluminum hydroxide begins to cloud the solution. This will occur when about 45 c.c. of acid have been dropped in. Now add the acid $\frac{1}{2}$ c.c. at a time, stirring thoroughly, until turmeric paper is no longer

turned, quickly, to even a faint brown by the solution. The solution will still be somewhat alkaline, but it is essential to a good separation that it be so. Very small amounts of aluminum hydroxide settle slowly, requiring several hours to collect, and giving, at first, only a faint cloudiness in the solution. Mix with the precipitate a quantity of paper pulp about equal to the volume the precipitate would occupy if it were drained on a filter. A wad about the size of a large walnut is sufficient in most cases. Wash with ammonium nitrate water (1 gram of the salt dissolved in 100 c.c. of water). If the mixture of pulp and aluminum hydroxide, after being washed 15 or 20 times, is not entirely free of yellow tint, it should be dried; the paper burned off in the platinum crucible and the residue fused once more with Na_2CO_3, only, and treated exactly as before, i.e., dissolved in water; filtered; washed; and the filtrate precipitated with 1 : 1 hydrochloric acid. This insures a snow white precipitate, free of vanadium. The aluminum hydroxide being now free of vanadium is dissolved off the filter with 50 c.c. of hot 1 : 1 hydrochloric acid. The hot acid is poured on the pulp six times, reheating the solvent at each pouring. The paper pulp is washed free from chlorides with water. The filtrate and washings are heated to boiling, and the aluminum hydroxide is precipitated in the usual way with a slight excess of ammonia, paper pulp added and the hydroxide washed, roasted and blasted to a constant weight as $Al_2O_3 + P_2O_5 + SiO_2$.

Test all of the filtrates mentioned in the foregoing outline by adding an excess of acid and then a slight excess of ammonia to make certain that the various manipulations have been properly conducted.

The writer has repeatedly observed in making the separation of much aluminum from much, or indeed any, vanadium that if the neutralization of the hot sodium carbonate fusion be carried farther than here given the

aluminum hydroxide will contain vanadium. In short, make sure that the solution is still distinctly alkaline. To guard against presence of silica it is well to add 10 c.c. of hydrofluoric acid and a few drops of sulphuric acid to the $Al_2O_3 + P_2O_5 + SiO_2$. Evaporate; ignite; and weigh again.

The phosphorus in the precipitate is estimated and deducted as follows: Fuse the precipitate with 10 grams of sodium carbonate; dissolve in water; precipitate with 1 : 1 HCl as described; dissolve off the filter with 50 c.c. of hot 1 : 1 hydrochloric acid and wash free of chlorides as usual. Evaporate to 5 c.c.; add 100 c.c. of concentrated nitric acid; evaporate again to 10 c.c. Dilute with 20 c.c. of water; filter through a small filter and wash with very dilute nitric acid. Evaporate the filtrate and washings to 50 c.c.; boil with a slight excess of permanganate of potash; clear with a small excess of ferrous sulphate followed by an addition to the still hot solution of 50 c.c. of molybdate solution. Finish as in phosphorus in steels; calculate to P_2O_5 and deduct from the weight of silica free $Al_2O_3 + P_2O_5$. The remainder is the pure Al_2O_3. The acid precipitation of aluminum hydroxide is an application of the well-known reaction, Al (ONa)3 + 3 HCl = 3 NaCl + Al (OH) 3. Treadwell mentions that W. F. Hillebrand recommends this separation of aluminum from small amounts of vanadium found in ores of iron, and in rocks. The writer has never had the pleasure of reading Hillebrand's article. The reference is given as *American Journal of Science* (4), VI, p. 209.

Phosphorus.

Vanadium precipitates with the phosphorus if an attempt be made to determine the percentage of the latter element by a molybdate separation as ordinarily practiced in steel analysis. The phospho-molybdate is colored by presence

of vanadium, being of a rather dark orange color.   Further, in the presence of much vanadium most of the phosphoric acid is *not* precipitated by the molybdate solution as used in steels.

Having noted vagaries that have been commented on by several authors of works on the analysis of iron and steel, and not having read any suggestion that improved the situation, some experiments were made to study the matter.   First the boiling of the nitric acid solution of the alloy with a very slight excess of potassium permanganate and then clearing with just one drop of ferrous sulphate was tried that is a precipitation in the presence of *vanadic* acid.   Second, as before, except that a large excess of ferrous sulphate was added after boiling with permanganate, being a precipitation in the presence of *vanadyl* salt. These two conditions were further modified by varying the length of time between the addition of the molybdate solution and the subsequent filtering out of the yellow or, rather, red precipitate.   The discordant results are given in Table 1, together with the actual phosphorus as obtained by the writer's aluminate method (page 23).

From such results, and others not given, it was decided to remove the vanadium entirely from the phosphorus and then precipitate with molybdate.   As iron carries large quantities of vanadium with it when precipitated in the presence of the former element by ammonia, phosphorus could not be separated as ferric phosphate.   A number of other schemes were resorted to, and finally the following plan proved successful, and demonstrated, as given in the table, that as little as one-fourth of the phosphorus is, at times, obtained by the ordinary methods as given in the most recent books on the analysis of steel works materials.

A solution of sodium aluminate was prepared by placing 10 grams of metallic aluminum in a large dish (platinum preferred) together with 50 grams of stick caustic soda.

TABLE NO. 1.

Grade of Ferro-V. Per cent V.	Weight Taken, Grams.	Amount of Excess of Ferrous Sulphate.	Time Elapsing between the Addition of the Molybdate and the Filtering Out of the Phospho-molybdate Precipitate.	Phosphorus Found by the Several Variations of the Ordinary Method; and Color of Precipitate.	The Phosphorus as Found by the Author's Aluminate Method; and Color of Precipitate.
No. 124. 11% V.	0.815	None	1 hour	0.322% red	{0.427% phosphorus. / 0.404% / Bright yellow.}
No. 124	0.815	None	24 hours	0.214%	
No. 124	0.815	Large	24 hours	Very red	
No. 4. 52.50% V.	0.815	None	1 hour	0.060%	{0.242% / 0.258% / 0.247% / Bright yellow.}
No. 4	0.500	None	1 hour	0.062% red	
No. 4	0.815	Large	24 hours	{0.120% / 0.166%}	
No. 4	0.815	Large	24 hours	Very red	
No. 4	0.500	Large	1 hour	0.130% red	
No. 134. 57.5% V.	0.815	None	1 hour	0.036% red	0.233% / 0.234% / 0.236% / 0.235%
No. 134	0.815	Large	1 hour	0.022% red	
No. 134	0.815	None	25 hours	0.152%	
No. 134	0.815	Large	25 hours	0.122 / Very red	Bright yellow.

Water was added a drop at a time as the action proved extremely violent — much heat being generated. When the reaction was complete the mass of aluminate was dissolved in water; some paper pulp was added; the solution was filtered, and the filtrate and washings were diluted to 520 c.c.

A double fusion using 10 grams of sodium carbonate and 2 grams of potassium nitrate, each time, is made of 0.815 gram of the powdered sample in exactly the same manner as just described for the aluminum separation. Add to the combined filtrates and washings from the iron residue 5 c.c. of the sodium aluminate solution and precipitate it with 1:1 hydrochloric acid, adding the acid until the solution no longer changes turmeric paper, at once, to even a faint brown.

The precipitated aluminum hydroxide and phosphate are washed 15 times with ammonium nitrate solution, roasted in a platinum crucible, and fused again with 10 grams of Na_2CO_3 + 2 grams KNO_3. The melt is dissolved in water, filtered, and precipitated again with 1:1 hydrochloric as described under aluminum. This precipitate is then washed, converted into nitrate, and the phosphorus is separated with molybdate solution. It is a bright yellow, totally free of red tint. The extent to which vanadium holds phosphorus in solution is shown by the results obtained, which are also given in the table for convenient comparison. The United States Bureau of Standards pig iron "B" was dissolved in 1.20 nitric acid, evaporated, ignited to a dull red, dissolved in hydrochloric acid, precipitated with ammonia; washed; roasted in a platinum crucible and treated as though it were a ferrovanadium. The phosphorus was obtained by the aluminate and acid scheme. A laboratory standard was tested in like manner for phosphorus. The correct phosphorus was obtained in each sample.

Second Method for Aluminum and Phosphorus in Ferro-Vanadium.

Dissolve one gram of sample in 40 c.c. 1.20 nitric acid. If there remains an insoluble metallic residue when percentage of silicon is high, filter out the undissolved part. Wash it with 1.20 nitric acid. Roast off the paper pulp. Fuse it with twenty times its weight of Na_2CO_3 plus one-fifth its weight of potassium nitrate. Dissolve the melt with water in a platinum dish. Transfer the water solution to a porcelain dish; add an excess of 1:1 hydrochloric acid. Heat until all is dissolved. Clean the crucible with 1:1 hydrochloric acid when all is in solution. Transfer the acidulated fusion and the cleanings of the crucible to a 1000 c.c. boiling flask. Also add to the same, the filtrate and washings from the residue that remained undissolved in nitric acid. Dilute to about 300 c.c. Hold the flask in one hand, and project into it with the other hand from a small porcelain spoon, sodium peroxide, a gram or two at a time. When sufficient peroxide has been added to precipitate all of the iron, then add an excess of 10 grams of the former; also 10 grams of sodium carbonate to supply carbon dioxide. Boil twenty minutes; cool and filter out the iron hydroxide, mixing with it a large amount of paper pulp. Wash this mixture on the filter with sodium carbonate water twenty times. The filter should be a double 12 cm. one. The strongly alkaline solution is diluted with 100 c.c. of water before the iron hydroxide is filtered from it. Each washing is well drained off before the next one is added. A small square of cheese cloth is folded in with the filter at the apex to prevent the alkaline solution from tearing the paper. This filtrate and washings are designated A.

Dissolve the iron residue off the filter and treat it with peroxide and 10 grams of carbonate exactly as before, obtaining filtrate B.

Phosphorus.

(A) Heat the filtrate and washings from the iron hydroxide obtained in the first peroxidation; add 5 c.c. of the aluminate solution. Mix well. Then introduce 1 : 1 hydrochloric acid as described in the first method for phosphorus. Keep the solution slightly but distinctly alkaline. The acid is added until the solution no longer gives turmeric paper a *faint* brown tint, *quickly*. Filter off the aluminum hydroxide, mixing paper pulp with it. Dissolve the hydroxide off the filter with 40 c.c. of 1:1 hydrochloric acid, after first washing 15 times with ammonium nitrate water. Pour the hot acid back and forth over the pulp six times, heating the acid before each pouring. Wash the pulp free from chloride test with water.

The filtrate and washings from the pulp are peroxidized, also. This time add only enough peroxide to insure alkalinity and to dissolve any aluminum hydroxide that may appear. Boil the solution 10 minutes, adding 10 grams of sodium carbonate before boiling. Remove from the flame and precipitate as before with 1 : 1 HCl. Filter off aluminum hydroxide and finish as given for phosphorus in the first method. Add a slight excess of acid to the filtrate and washings; then a faint excess of ammonia to make sure that all aluminum hydroxide has been precipitated. The aluminum hydroxide is put through this second peroxidation to remove any vanadium that is carried down with it the first time it is precipitated with acid. It should now look pure white, free from any suggestion of yellow tint. If it has a yellow color, too much acid has been used in its precipitation. In that event it must be dissolved off the filter and peroxidized again, but unless proper degree of alkalinity is observed it will still appear yellow.

(B) The filtrate and washings from the second peroxida-

tion of the iron are treated with 5 c.c. of aluminate solution and then as described for those obtained from the first peroxidation; but as practically no vanadium is present in the second peroxidation, this aluminum hydroxide is free of any vanadium and can be dissolved off the filter and converted into nitrate at once to obtain the remainder of the phosphorus.

(C) The iron residue after its second peroxidation is dissolved off its filter with hot 1.20 nitric acid, pouring the acid back on the filter six times, stirring up the pulp each time with a glass rod. Wash 40 times. Evaporate filtrate and washings to 40 c.c. Boil with permanganate and finish as in steels. Only a few thousandths of a per cent of phosphorus are found with the iron, even with a phosphorus content of 0.24 per cent.

This method avoids all fusions except one, and that one is necessary only in high silicon ferros. It checks perfectly with the first method and is really an outgrowth of it. However, it requires more of the operator's time in that he cannot give his attention to much else while making the peroxidations. It is an economy of platinum rather than of time.* If, after removing the vanadium by either the first or second methods for phosphorus, the phospho-molybdate still retains an orange shade rather than a light canary yellow, vanadium is still present to some extent, and a considerable portion of the phosphorus is surely held in solution. It means that some part of the directions have not been exactly followed. The trouble is almost certain to be due to having precipitated the aluminum hydroxide in too faintly alkaline solution. For example, if the color of the phospho-molybdate suggests even a slight red and the precipitate tends to adhere to the bottom of the beaker, a result of 0.19 per cent may be obtained when the actual phosphorus is 0.25 per cent.

* It can be used to advantage when a number of samples are assayed at the same time.

As the amount of phosphorus remaining with iron after the first peroxidation is very ·trifling for all practical purposes, it is not necessary for steel works, or indeed most technical analysis, to make a second peroxidation of it. In this way it is simply necessary to make the one peroxidation to remove iron, and the total phosphorus is then separated from the vanadium in the filtrate as given.   However, should more than 0.25 per cent phosphorus be found, it would be safer to follow the entire method as first described.

Add 0.100 gm. of aluminum dissolved in hydrochloric acid or 5 c.c. of aluminate solution for every 0.25 per cent of phosphorus supposed to be present in the ferro.

ALUMINUM.

Proceed exactly as for phosphorus, but add no aluminate.   Any precipitate that forms with 1 : 1 HCl is then treated as described in the first method for aluminum.   This process avoids all fusions except the one required when silicon is high.   A blank must be run, imitating the test in every detail.   A plain carbon steel can be used for the blank, weighing out approximately as much of it as there is supposed to be iron present in the ferro.   This separation of aluminum from vanadium and iron has been tested by the author with mixtures containing as much as 10 per cent of aluminum and 50 per cent of vanadium, the remainder being iron, on a one-gram basis.

A good way to run a blank for either aluminum or phosphorus is to dissolve 100 mg. of metallic aluminum of known aluminum content in a few c.c. of hydrochloric acid.   Add this to 400 mg. of a plain carbon steel.   Put the mixture through the entire analysis.   Deduct the excess of aluminum found from the aluminum obtained from the ferro.   The remainder will be the aluminum sought in the

ferro-vanadium.*   Deduct the phosphorus found in this blank test from that found by the same process in the ferro, allowing for the phosphorus known to be in 0.400 gram of steel used.

Instead of using the aluminate solution for the phosphorus determination, 100 mg. of aluminum can be added, after dissolving it in a few c.c. of 1:1 hydrochloric acid, whenever the foregoing directions call for 5 c.c. of aluminate.   In this way the aluminum and phosphorus can be gotten from the same analysis.   It is merely a matter of deducting from the total aluminum found, the aluminum added, and also the blank.   Add 100 mg. of aluminum dissolved in hydrochloric acid for every 0.25 per cent of phosphorus when one gram of sample is taken for analysis. The phosphorus is gotten last by fusing the $Al_2O_3 + P_2O_5$ after it has been weighed in the silica free condition. Fuse the oxides with sodium carbonate, using ten grams. Dissolve the melt in water.   Precipitate the water solution as usual with 1:1 hydrochloric acid.   Filter off the aluminum hydroxide, etc.   Wash it a few times.   Mix paper pulp with the hydroxide to hasten filtration and washings.   Dissolve the hydroxide off the filter with 50 c.c. 1:1 hot hydrochloric acid as previously described in the first method.   Wash the pulp free of chlorides.   Evaporate the filtrate and washings to about ten c.c.   Add 100 c.c. of conc. nitric acid and evaporate to 15 c.c.   Rinse into a 5 oz. beaker.   Boil with permanganate solution and finish as in steels.

As considerable silicic acid is obtained from the operations in this second method, it is better to remove the silicon by evaporating the aluminum chloride, etc., to dryness just before precipitating it to weigh it

* For example if 0.100 gm. of 99.5 per cent aluminum is added to 400 mg. of a plain steel and 0.110 gm. is recovered by the method, then the blank would be 0.110 — 0.0995 or 0.0105 gm.

as $Al_2O_3 + P_2O_5$. This avoids the use of hydrofluoric acid.

A single peroxidation is not sufficient to separate the aluminum from the iron. A little is always found in the filtrate from the iron hydroxide after its second peroxidation.

Iron.

The iron residue obtained from fusions for aluminum or phosphorus is roasted free of paper; dissolved with hydrochloric acid. The crucible in which the fusions were made is cleaned by warming a little of the same acid in it. The cleanings are added to the main solution of the residue. Sixty c.c. of 1:3 sulphuric acid are introduced, and the solution is evaporated to thick fumes. The residue is dissolved in 300 c.c. of water, and hydrogen sulphide is passed through it until the various sulphides have settled out well. The reduced iron is filtered free of sulphides into a round flask. Hydrogen sulphide is again passed through the solution to reduce any iron that may have become oxidized during filtering and washing. The hydrogen sulphide is removed by boiling the solution with carbon dioxide passing rapidly through it. When the gases coming from the hot flask no longer cause filter paper moistened with lead acetate to turn brown or black, the flask is cooled in water with carbon dioxide still passing. When cold the solution is titrated with a potassium permanganate standard 1 c.c. of which equals 0.00556 gram of .iron made by dissolving 3.16 grams of c.p. permanganate in water and diluting to one liter. (See Standardization of $KMNO_4$, page 45.)

The writer frequently uses the plan of dissolving the ferro in sulphuric and nitric acids, with a little hydrofluoric acid if necessary. Evaporation to fumes and solution in water are the next steps. The vanadium and iron

are then reduced with hydrogen sulphide, the solution filtered, hydrogen sulphide removed with CO_2, and permanganate of potash standard is added until a pink is obtained or an old-rose shade, that does not fade perceptibly after one minute's stirring. 1.2 c.c. of ferricyanide indicator are now dropped in, and a ferrous ammonium sulphate standard, 1 c.c. of which equals 1 c.c. of the permanganate, is added until three drops of this standard cause the light blue of the vanadyl solution to darken with the blue of the ferricyanide of iron. The number of c.c. of permanganate used to produce the old-rose shade less the number of c.c. of sulphate required, equals the number of c.c. of permanganate used to oxidize the iron, which number multiplied by 0.00556 gives the amount of iron in parts of a gram. The number of c.c. of sulphate used to produce a darkened blue, multiplied by 0.00508 (provided the sulphate exactly equals the permanganate), equals the number of grams or parts of a gram of vanadium present.

The iron residue from the carbonate and niter fusions may be proceeded with for the estimation of the latter metal in this way: After removing the platinum, copper, etc., from the hydrochloric acid solution of the iron oxide by hydrogen sulphide, evaporate the filtrate and washings from the sulphides with a small excess of potassium chlorate. Remove the hydrochloric acid by evaporation to thick fumes with 60 c.c. 1:1 sulphuric acid. Add water; dissolve by heating; reduce with metallic zinc, and titrate with standard permanganate for iron.

COPPER.

If copper is present to any appreciable extent, as shown by the clouding with the ferricyanide indicator, it can readily be separated by hydrogen sulphide, passing the latter gas through the sulphate solution obtained by dis-

solving the sample in nitro-sulphuric acid, using a little hydrofluoric acid if much silicon be present, evaporating to fumes of sulphuric acid and dissolving in boiling water to hasten solution. (Copper can also be easily and quickly separated from this sulphate solution by neutralizing most of the free acid and precipitating the copper with an excess of potassium thiocyanate and sulphurous acid. (Also see the author's ferricyanide separation.) The sulphide of copper is filtered, washed with hydrogen sulphide water, roasted free of paper in a porcelain crucible, dissolved in 1.20 nitric acid, filtered from any insoluble sulphides or alumina. The filtrate and washings are made slightly alkaline with sodium carbonate water; one c.c. of ammonia is added and the solution titrated to disappearance of a blue with potassium cyanide standardized against 99.8 per cent metallic copper in the same manner.

Chromium, as already intimated, when present, can be determined in the presence of vanadium and in the same operation.

In steels the amount of double sulphate used to discharge all red colorations leaving the solution a clear light green, free of all yellowish tints, less the number of c.c. of the permanganate standard required to produce a slight permanent pink reflection, thereafter, equals the amount of double sulphate necessary to reduce the chromic acid present to chromic sulphate. One c.c. of the double sulphate usually equals 0.00087 gram of chromium. As already explained, the ferricyanide indicator is now dropped in, and the sulphate standard again follows until three drops of it produce a dark green. The amount of sulphate consumed by this last titration is equivalent to the vanadic acid present, after deducting the regular blank, which is usually 0.4 to 1.0 c.c., depending on the amount of chromium. A sample calculation is given as an illustration.

FIRST PART OF THE TITRATION TO OBTAIN THE CHROMIUM.
(MADE BEFORE ADDING FERRICYANIDE.)

KMnO$_4$		Double Sulphate.
9.1 c.c.	second reading of burette	28.6 c.c.
2.3 c.c.	first reading of burette	12.4 c.c.
6.8		16.2

CALCULATION.

16.2
6.8

9.4 c.c. equal sulphate used by chromium.

9.4 × 0.00087 × 100 ÷ 2 = 0.4089, or per cent chromium.

SECOND PART OF THE TITRATION (MADE IMMEDIATELY AFTER
ADDING THE FERRICYANIDE INDICATOR) TO OBTAIN THE
VANADIUM.

Sulphate.

31.4 c.c. second reading of burette.
28.6 c.c. first reading of burette.

2.8
.4 equals regular vanadium blank for low per cent chromium.

2.4

Since 1 c.c. of sulphate equals 1 c.c. of permanganate or
0.00254 gram of vanadium, therefore 2.4 × 0.00254 × 100
÷ 2 = 0.305 per cent vanadium.

Small Amounts of Chromium.

Ferro-vanadium frequently, as stated, contains one or
two tenths of a per cent of chromium. The most satisfac-
tory way to estimate these small amounts, in the presence
of large per cents of vanadium, is to fuse 1 gram of the
finely ground powder or thin drillings with 20 grams of
sodium carbonate and 4 grams of niter. After the
fusion is quiet, keep it molten for thirty minutes. Dissolve
the melt in as little water as possible in a platinum or
porcelain dish. Add pulp; filter; wash with sodium car-
bonate water. Evaporate the filtrate and washings to

about 40 c.c.   If the solution is not clear, add a little pulp, filter and wash again.   The filtrate and washings should not exceed 40 to 50 c.c. if the chromium content is only a tenth of a per cent or thereabout.   Compare this solution with a standard consisting of 0.070 gram of c.p. potassium dichromate made slightly alkaline with sodium carbonate and diluted to 250 c.c. in a volumetric flask.   It is made alkaline by adding sodium carbonate until the red color of the dichromate has all been converted into the yellow of the sodium chromate.   1 c.c. equals 0.0001 gram of chromium. Use the same comparison tubes as described under the color method for titanium.   Rinse one of the tubes three times with some of the standard.   Then pour into it exactly 10 c.c. of the standard solution.   If the chromium content is about 0.20 per cent, the standard will be yellower than the test.   Add water to the standard, 1 to 2 c.c. at a time until its color is only slightly stronger than that of the test.   Continue the addition of water in $\frac{1}{2}$ c.c. amounts until the standard is just turned lighter than the test. Suppose the standard matches the test in color at 27.5 c.c. and the volume of the test is 59.5 c.c.   This gives the proportion:

Standard Vol.   Test Vol.   10 c.c. Std.
   27.5   :   59.5   : :   0.001   : X

$5.95 \div 27.5 = 0.21$, or 0.21 per cent chromium.

MOLYBDENUM.

Molybdenum is separated exactly as the copper with hydrogen sulphide in slightly acid solution.   The brown sulphide is roasted at a low heat in a porcelain crucible to a white or a bluish-white residue (unless dark colored oxides are present, such as copper).   The white oxide is brushed into a platinum crucible, fused with ten times its weight of sodium carbonate; dissolved in water; two drops

of methyl orange are added, and then hydrochloric acid until one drop produces a pink. Add 1 c.c. of conc. hydrochloric acid in excess. Heat the solution to boiling. Precipitate the molybdenum in the hot solution with lead acetate. Add also an equal volume of a solution of ammonium acetate (50 grams of the salt made to a volume of 100 c.c. with water). Let the precipitate settle for an hour or two. Cool. Filter. Wash with hot water. Ignite in a platinum crucible at a low red-heat. Cool and weigh as lead molybdate, which multiplied by 26.16 and divided by the weight taken for analysis gives the per cent of molybdenum. See Molybdenum in Steel, page 75.

SILICON.

For silicon dissolve one gram of the finely ground ferro in 50 c.c. 1.20 nitric acid. Add 30 c.c. 1.3 sulphuric acid and evaporate to fumes. Dissolve the sulphates in water, heating until all but silicic acid is in solution. Filter. Wash with dilute hydrochloric, then with water. Ignite and weigh as usual. If the sample contains much silicon and does not yield to the nitric acid, filter out the insoluble residue; wash it first with hydrochloric acid and then with water; roast off the paper in a platinum crucible. Fuse the residue with 20 times its weight of sodium carbonate plus ⅕ its weight of potassium nitrate. Dissolve the melt with water. Acidulate it with hydrochloric acid and add the clear solution to the portion dissolved by the nitric acid, and evaporate all to fumes with 30 c.c. of 1 : 3 sulphuric acid, and finish as in low silicon ferro-vanadium.

STANDARDIZATIONS.

The writer prefers to standardize permanganate of potash against recrystallized oxalic acid kept in tightly stoppered bottles: 1.58 grams of potassium permanganate are dis-

solved in a liter flask with distilled water and diluted to the mark.   19.5815 grams of double sulphate of iron and ammonia, i.e., $FeSO_4$, $(NH_4)_2 SO_4 + 6 H_2 O$, are dissolved in the same manner, with the addition of 50 c.c. of 1 : 3 sulphuric acid, and diluted to one liter.   Usually the relationship between these two standards is 40.2 to 40.5 c.c. of the permanganate equals 40 c.c. of the double sulphate. The vanadium value of the permanganate standard is checked against the oxalic acid, and the vanadium value of the sulphate standard is calculated from its relation to the permanganate standard.

The 1.58 grams of permanganate solution, theoretically, should be equivalent to 2.56 grams of vanadium.   Its actual value is found as follows: 0.1424 gram of oxalic acid are dissolved in about 100 c.c. of water plus 20 c.c. of 1 : 3 sulphuric acid and heated to 80° C.   The permanganate standard is then added until one drop produces a permanent pink.   This usually requires 45.45 c.c. of the permanganate. We in first place have the proportion:

Oxalic Acid.		Permanganate.				
63	:	31.6	: :	0.1424	:	X.

This gives X equals 0.07142, or 0.07142 gram of pure permanganate will oxidize 0.1424 gram of oxalic acid.   By the above titration it is found that it requires 45.45 c.c. of the permanganate standard to oxidize 0.1424 gram of oxalic acid.   Therefore each c.c. of the permanganate standard must contain 0.07142 divided by 45.45, or 0.001571 gram of 100 per cent potassium permanganate.   We thus obtain the final proportion, or

$$1.58 : 2.56 : : 0.001571 : X.$$

X equals 0.002545, or 1 c.c. permanganate solution equals 0.002545 gram of vanadium.

The chromium value of these standards is found by adding to two grams of a plain carbon steel a weighed

amount of recrystallized potassium dichromate. This mixture is put through the entire process of an analysis. Taking the percentage of chromium in dichromate of potash as 35.38 per cent, the sulphate standard is found to have a value that varies from 0.00085 to 0.00087 gram of chromium per c.c.

It must be constantly borne in mind that to attain success in vanadium and chromium titrations, in steels, that it is absolutely essential when coming back with permanganate to stop with the first three drops that give a faint pink reflection that is still faintly, but distinctly, visible after *thirty seconds* stirring.   Furthermore, the next step is to add the ferricyanide indicator.   Then the ferrous ammonium sulphate is quickly added until three drops produce the first distinct darkening of the green.   Do not continue to add the sulphate to a still darker green, or, worse, to a blue.   In short, if the pink end-point is overdone, and then the green one also, the error is doubled.   Always aim to finish standards, blanks, and tests exactly as described.

The author has had occasion to analyze the following varieties of ferro-vanadium which will give some idea of the different types likely to be encountered by the iron and steel analyst:

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Vanadium................	22.77	12.45	35.15	52.5	31.48	23.33
Carbon...................	1.74	0.16	0.35	3.09	0.08	4.55
Manganese...............	0.07	0.46	0.10	0.07	0.28	3.30
Phosphorus..............	0.40	.....	.....	0.28	.....	.....
Silicon	0.60	7.65	1.02	0.43	13.00	3.8
Iron.....................	74.08	65.54	62.60	41.50	.....	.....
Sulphur	.....	0.15	.....	0.52	.....	.....
Chromium...............	.....	.....	.....	0.22	.....	.....
Aluminum................	.....	7.31	.....	.....	4.13	.....
Copper...................	.....	6.24	.....	.....	.....	.....
Molybdenum..............	.....	.....	.....	0.50	.....	.....

CHAPTER III.

FERRO-TITANIUM AND TITANIUM STEEL.

SOLUBLE FERRO-TITANIUM.

Titanium. When ferro-titanium of low titanium content, 8 per cent titanium for example, dissolves almost completely in sulphuric acid, proceed in the following manner: Dissolve 0.4 to 0.5 gram of drillings in 30 c.c. 1 : 3 sulphuric acid. Filter and keep the insoluble residue if any. After washing it free from blue iron test with potassium ferricyanide, it is fused with twenty times its weight of sodium carbonate. (Use 1 : 10 sulphuric acid for washing.)

Nearly neutralize the filtrate and washings with 1 : 3 ammonia water. Dilute to 300 c.c. with water. Add to the cold solution 5 grams of sodium thiosulphate* dissolved in water. Boil gently for half an hour, and filter, using paper pulp. Wash with sulphurous acid water (2 c.c. of conc. sulphurous acid to 500 c.c. of water) until no test for iron is obtained. The washed precipitate is ignited and fused with twenty times its weight of sodium carbonate. Keep the fusion molten at a bright red-heat for forty minutes. Dissolve in water in a platinum dish; add ashless paper pulp; filter; wash thirty times with sodium carbonate water. Heat the filtrate to boiling in a beaker; add hydrochloric acid drop by drop to the filtrate, and note if a white precipitate forms at any time before the filtrate becomes acid. If a precipitate forms, then roast the sodium titanate to

* That is, 5 grams of "thio" for every 50 mg. of Ti likely to be in the solution.

free it from pulp, and fuse again as before; filter; wash; and treat the aluminum-free titanate as follows:

* Spread filter and residue in a small dish and cover it with about 30 c.c. of 1 : 3 sulphuric acid.   It is heated on a water bath for a half-hour, or until all but the filter pulp is in solution.   The pulp is filtered out and washed thirty times with dilute 1 : 20 sulphuric acid water and then with water until the washings no longer show a test for sulphuric acid with barium chloride solution.   Burn this washed pulp to make sure that all titanate is dissolved.   The filtrate and washings are nearly neutralized with ammonia; five grams of sodium thiosulphate are added, and the titanic acid is precipitated and washed as before with sulphurous acid wash.   It is given forty washings and ignited and weighed as TiO_2 plus a little SiO_2.   The residue is treated with 5 to 10 drops of conc. sulphuric acid.   The crucible is filled about three-fourths full of c.p. hydrofluoric acid and freed from silica as in steels.   The weight thus obtained being the pure TiO_2 is multiplied by 60 and divided by the weight taken for analysis to obtain the percentage of titanium.

The small insoluble residue obtained from the first solution of the drillings in 1 : 3 sulphuric acid is fused with twenty times its weight of sodium carbonate.   The melt is dissolved in water; washed thirty times with sodium carbonate water.   The filter and residue are spread out in a small dish with 20 c.c. 1 : 3 sulphuric acid and heated on a water bath for thirty minutes to dissolve the titanate of soda.   The paper pulp is then removed by filtration, and the filter is washed thirty times with 1 : 20 sulphuric acid. The filtrate and washings from the pulp are made nearly neutral with ammonia water; five grams of "thio" are

* Or the filter and residue can be roasted; fused with 10 gms. of $KHSO_4$; the melt dissolved; filtered; the filtrate and washings nearly neutralized and the Ti precipitated as before with "thio."

added, and the solution is boiled gently for half an hour. The titanic acid thus obtained is combined with the main precipitate obtained in like manner with sodium thiosulphate. It is roasted with it just before it is fused the first time with sodium carbonate to remove alumina.

Sulphur, Phosphorus, and Aluminum* in Ferro-Titanium.

The sulphur, phosphorus, and aluminum in all varieties of ferro-titanium can be best obtained by fusing the drillings or powdered material in a platinum crucible with twenty grams of sodium carbonate ground thoroughly with four grams of potassium nitrate. A double fusion should be made. Fuse one gram of sample as above. When the melt is in a state of quiet fusion, keep it at a bright red-heat for 30 minutes longer. Dissolve the fusion in a porcelain or platinum dish in hot water. A platinum dish is best for this work. If the supernatant fluid in the dish is tinged with green, or in high per cents of manganese from 1 per cent and above is a deep green, then add a few drops of absolute alcohol which will convert the green manganate of soda into the brown oxide of manganese. Continue to warm the solution until all green color is gone and the liquid is colorless. This procedure leaves all of the manganese with the iron and titanium. Wash the residue with sodium carbonate water. Roast it; fuse again; dissolve; treat with alcohol; filter; wash and combine the two filtrates and the washings in one beaker. Add to this solution, which contains all of the sulphur, phosphorus, and aluminum in the alloy, 1:1 hydrochloric acid until the solution is slightly acid. Heat to boiling. Add a slight excess of ammonia which will precipitate all of the aluminum as hydroxide and phosphate. This pre-

* Aluminum can also be obtained as given on page 25, except that the ferro is dissolved in H_2SO_4.

cipitate, if present in considerable quantity, will carry all of the phosphorus present in the ferro. It is washed with ammonium nitrate water and dissolved off the filter at once with hot 1:1 hydrochloric acid. The filter is washed free of acid and should be burned, weighed, and its weight added to the final weight of the $Al_2O_3 + SiO_2$.

It is claimed that aluminum precipitated from solutions containing sodium chloride carries with it a certain amount of soda salt that cannot be removed from it by wash water. This is why the aluminum hydroxide is redissolved in 1:1 hydrochloric acid. It is then precipitated hot with ammonia in slight excess and washed with ammonium nitrate water; ignited and weighed, as $Al_2O_3 + P_2O_5 + SiO_2$. The silica is removed by hydrofluoric acid and a few drops of sulphuric acid as usual, and the residue is ignited and weighed again as $Al_2O_3 + P_2O_5$. This residue is fused with twenty times its weight of sodium carbonate. The melt is dissolved in water; acidulated with nitric acid in slight excess. The volume is made up to 50 c.c.; boiled with $KMnO_4$, and the phosphorus precipitated as usual with molybdate solution. The number of milligrams of phosphorus found is calculated to percentage and also to P_2O_5. The milligrams of the latter are deducted from the weight of $Al_2O_3 + P_2O_5$ and the remainder is multiplied by 53.03 and divided by the weight taken for analysis to obtain the percentage of aluminum in the alloy. (See page 188, Phosphorus in Graphite.)

If the original filtrates from the double fusion show very little or no aluminum on being treated with hydrochloric acid until the hot solution is only faintly alkaline, then there is a possibility that the filtrate from this aluminum may still contain phosphorus. To obtain this phosphorus a solution of ferric chloride free of phosphorus and sulphur is added to the filtrate from the small quantity of

aluminum or to the slightly acid solution, if no aluminum hydroxide formed.

This solution, which should be faintly colored with ferric chloride and slightly acid, is precipitated hot with a small excess of ammonia. The precipitate is filtered out; washed with hot water; is dissolved off the filter with a little hot 1.20 nitric acid. The filter is washed free of iron test, using potassium sulphocyanate for the detection of iron in the washings. The dilute nitric acid wash water is used. (See Phosphorus in Steel, page 164.) Concentrate the filtrate and washings to 40 c.c. Boil with a little permanganate; clear with ferrous sulphate and finish as in steels. The phosphorus found in the iron precipitate plus that found with the aluminum hydroxide, if any formed, equals the total phosphorus in the ferro.

The filtrate from the aluminum hydroxide, or iron hydroxide, or both, is made slightly acid with hydrochloric acid and evaporated to dryness in a 600 c.c. casserole. Ten c.c. of 1:1 hydrochloric acid are added to the dry residue. It is heated with a cover on the dish; 200 c.c. of water are added, and the dish is heated nearly to boiling, or until all of the salt is dissolved. The solution is filtered. The filter is washed with 1:10 hydrochloric acid. The filtrate and washings are precipitated with 20 c.c. of a saturated solution of barium chloride. The barium sulphate formed is allowed to settle twelve hours. It is filtered with a little pulp; washed free from chloride test with water only; burned in a weighed platinum crucible; moistened with a drop or two of 1:3 sulphuric acid, as the burning of the paper always reduces a little of the barium sulphate to $BaSO_3$. It is ignited again and weighed as $BaSO_4$, which weight, multiplied by 13.73 and divided by the weight taken for analysis, gives the percentage of sulphur in the sample. Deduct a blank due to the fluxes

and acids used.   Blanks should always be made, as sodium
carbonate and acids are liable to contain sulphates, iron,
and aluminum.

Iron in Soluble Ferro-Titanium.

Dissolve 0.5 gram of sample in 1:3 sulphuric acid.   If
there be any insoluble residue that is not white, filter the
same out and wash it with dilute sulphuric acid.   Roast
it.   Fuse it with potass. bisulphate.   Dissolve the melt in
dilute sulphuric acid and add it to the filtrate and wash-
ings from the insoluble residue.   Dilute the slightly acid
filtrate and washings to 200 c.c.   Pass hydrogen sulphide
through the same until the iron is entirely reduced.   It will
be colorless when hot.   The reduction will take about an
hour, with the gas passing at a rather rapid rate.   Filter
the solution into an 800 c.c. boiling flask.   Wash the filter
with 1:10 sulphuric acid until free of iron test.*   Pass
hydrogen sulphide through this filtrate for one hour more.
(Saturate the acid wash with H_2S before using.)

Now pass a stream of carbon dioxide through the solu-
tion, keeping the same at boiling temperature during the
time that the CO_2 is passing.   When a piece of filter paper,
moistened with a water solution of lead acetate, is no
longer discolored, even slightly, when held in the neck of
the flask, the excess of hydrogen sulphide is all driven out.
Place the flask in cold water with the stream of carbon
dioxide still passing through it.   The glass tube that carries
the H_2S and CO_2 into the fluid should, of course, reach
nearly to the bottom of the boiling flask.   When the con-
tents of the flask are cold, titrate with standard perman-
ganate of potash until one or two drops yield a pink
color that is permanent for several minutes.   The same

* The residue on this filter will contain all of the copper present
which can be roasted and finished as in steels for Cu.

standard that is used for titrating iron in ferro-vanadium can be utilized in this determination. One c.c. of the standard equals 0.00556 gram of metallic iron.

Manganese in Ferro-Titanium Soluble in Sulphuric Acid.

Dissolve 0.100 gram in 10 c.c. 1:3 sulphuric acid. Add 10 c.c. concentrated nitric acid. Boil off red fumes. Dilute to 35 c.c. with water and finish as in steels. This applies to manganese not in excess of 1 per cent. Use 0.05 gram for manganese content exceeding 1 per cent. Accurate to 2 per cent Mn. For higher percentages of manganese dissolve one gram of sample in 30 c.c. 1:3 sulphuric acid. Oxidize by boiling with 10 c.c. conc. nitric acid and one gram of potassium chlorate. Add 60 c.c. 1:3 sulphuric acid and evaporate to thick fumes. Cool, add water and heat till all is dissolved except perhaps some of the titanic oxide and silicic acid. Be sure that all iron and manganese sulphates are in solution. Wash the cold solution into a liter flask. Fill the flask one-half full with distilled water. Add a rather thick paste of manganese-free zinc oxide and distilled water. Continue the addition of the zinc oxide until the iron and titanium settle out well, avoiding any unnecessary excess of the zinc oxide. Cool, if necessary, to the temperature of the room, and dilute the contents to the liter mark with distilled water. Mix ten times, inverting the stoppered flask each time.

Permit the precipitate to settle for a half-hour with the flask in an inclined position. Pour the supernatant fluid through a large, dry filter into a dry beaker. Use two filters to hasten matters. Rinse a hundred c.c. pipette three times with portions of the filtrate. Then draw out a 300 c.c. portion and a 400 c.c. portion. Place these

in separate boiling flasks, labeling them 300/1000 and 400/1000, respectively. Add two drops of 1.20 nitric acid to each of these aliquot parts. Heat the 300 c.c. to boiling, and titrate with standard permanganate of potash, adding a little at a time. Shake thoroughly with each addition of the permanganate solution, reheating the solution between times. When three drops finally produce a slight but distinct pink color in the hot supernatant fluid, after a reheating and thorough shaking, the end point is reached. Deduct 0.2 c.c. from the total permanganate used. Multiply its value per c.c. in milligrams of iron by 0.2945 to find its value in milligrams of manganese.

Titrate the 400 c.c. part in like manner and average the two results, calculating them as 3/10 and 4/10 of a gram, respectively. See also Mn in Insoluble Fe Ti.

Standardization of the Permanganate Solution for Iron and Manganese.

Weigh 3.16 grams of c.p. potassium permanganate crystals into a liter flask. Dissolve in distilled water and dilute to liter mark.

Weigh 0.2850 gram of c.p. recrystallized oxalic acid into a 200 c.c. beaker. Dissolve the crystals in 100 c.c. of hot water. Add 30 c.c. 1:3 sulphuric acid and titrate this hot solution with the permanganate solution. This latter should not be standardized for, at least, twelve hours after it has been dissolved and made up to 1 liter.

This amount of oxalic acid will require usually 45.50 c.c. of permanganate of the above strength to render it a faint pink that is permanent for several minutes. As the oxalic value of a permanganate solution multiplied by 8/9 gives its iron value therefore the latter is found by this calculation: $0.2850 \div 45.50 \times 8/9 = 0.005567$, or 1 c.c. of the permanganate equals 0.005567 gram of metallic iron. This value

multiplied by 0.2945 yields the value of the same solution in grams of manganese, or $0.005567 \times 0.2945 = 0.001639$ gram of manganese.   For check 0.280 gram oxalate took 44.8 c.c. $KMnO_4$, or $0.280 \div 44.8 \times 8/9 = 0.005555$ and $0.005555 \times 0.2945 = 0.001636$, or 1 c.c. $= 0.001636$ gram of manganese.   Average iron value equals 0.00556 gram and average manganese value equals 0.001637 gram per c.c. Compare the theoretical factor for manganese with that found by standardizing the permanganate standard by putting a ferro-manganese, containing a known per cent of manganese, through the identical process of fusion with bisulphate; precipitation with zinc oxide, etc.   See Analysis of Ferro-manganese, page 119.

Silicon in Soluble Ferro-Titanium.

Dissolve one or two grams of drillings as in steels.   Evaporate to fumes of sulphuric acid.   Dissolve in water.   Filter, wash, ignite, weigh, evaporate with a few drops of conc. sulphuric acid, and the usual amount of hydrofluoric acid.   Ignite and calculate the loss of weight as silicon. Should a white coating appear on the lid of the crucible when the sulphuric acid is being driven off, it means that there has not been a sufficient amount of sulphuric acid added, some of the titanium having volatilized as fluoride.

In such event, repeat the analysis, using a little more sulphuric acid with the hydrofluoric acid.

Nickel, Vanadium, and Chromium.

These elements are determined in soluble Fe Ti as in V, Ni and Cr steels, see pages 8, 32, 33 and 104.   Mix considerable washed asbestos pulp with the slimy mixture of silicic and titanic acids before filtering out the excess of manganese oxide, in the Cr and V determinations. Add paper pulp and filter off the titanic acid, etc., before adding the citric acid, in the Ni analysis.

Carbon in Soluble Ferro-Titanium.

Some ferro-titaniums of low silicon content can be completely decarbonized at 950° C. in a fused silica tube with oxygen. See Electric Combustion Furnace, page 150. It is safer to burn the sample in red lead. Burn one or two grams of thin drillings or 30-mesh powder with four grams of red lead.

Insoluble Ferro-Titanium.

Carbon, sulphur, and phosphorus are determined as given in the analysis of soluble ferro-titanium.

Silicon and Titanium.

These elements are best separated by fusion of 0.5 gram of the finely ground substance with 15 grams of acid potassium sulphate in 40 c.c. platinum crucible. This fusion is highly satisfactory if conducted with a little experience. Heat the crucible very gradually at first, using the white flame of an argand burner. Keep the melt below redness until all of the water has been driven out of the flux without sputtering. When slight fumes of sulphuric anhydride begin to make their appearance the heat can be increased to low redness. Maintain this temperature until the substance is in a state of clear fusion, and is a pure yellow, free of all black specks.

If the argand burner flame is properly adjusted, this operation can be going on with only occasional attention. When all black is gone, raise the heat until fumes of sulphuric anhydride come off briskly when the lid is lifted slightly.

Then turn off the heat and run the melt well up the sides. Place the crucible in a 250 c.c. casserole with 50 c.c. of water plus 50 c.c. of 1 : 3 sulphuric acid. Dissolve with

heat.   Filter out the white insoluble residue; wash it free of iron and sulphate, using barium chloride solution for the latter test and KCNS for the former.   Ignite it in a weighed crucible.   Weigh as SiO_2 plus a little TiO_2. Evaporate with HFl and a few drops of H_2SO_4 and calculate the loss of weight to silicon.   Keep the non-volatile portion to add to the main portion of TiO_2.

The filtrate and washings from the silica are made nearly neutral with ammonia and precipitated with thiosulphate of soda, and finished as in soluble ferro-titanium for Ti.

Iron.

Fuse 0.5 gram as for silicon.   Reduce with H_2S and finish as given under the soluble ferro.

Aluminum.

Proceed by fusion as given under aluminum in soluble ferro-titanium.

Manganese in Insoluble Ferro-Titanium.

If the percentage of manganese is under two per cent, fuse 0.100 or 0.05 gram with twenty times this weight of sodium carbonate and one-fifth that amount of potassium nitrate.   Dissolve the melt in a small porcelain dish with as little water as possible.   Clean the platinum crucible with a little hydrochloric acid; acidulate the water solution of the melt with the same acid.   Add to this solution the cleanings of the crucible and also 10 c.c. of 1:1 sulphuric acid.   Evaporate to thick fumes.   Dissolve the residue in water.   When the iron sulphate is dissolved, wash the solution into a 10 by 1 inch test tube and dilute to 20 c.c.   Add 10 c.c. of conc. nitric acid and finish as in steels.

For higher percentages of manganese proceed as given for high manganese in soluble ferro-titanium except that the substance is gotten into solution by a bisulphate fusion as given under the determination of silicon in insoluble ferro-titanium.   Transfer the sulphuric acid solution of the melt to a liter flask and precipitate the iron and titanium with zinc oxide.   Use 1 gram of sample and fuse it with 30 grams of bisulphate.

Titanium Steels.

For phosphorus, manganese, silicon, aluminum, and carbon, proceed as in plain steels if the titanium is present to the extent of a few tenths of a per cent.

Sulphur.

Even a few tenths of a per cent of titanium lead to low sulphur results by the evolution process.   For example, where results showing 0.006 per cent by evolution were obtained, 0.012 sulphur was gotten by the ordinary gravimetric sulphur method for steels.   Again, 0.075 per cent sulphur was gotten by evolution in a titanium experimental ingot when the gravimetric result was 0.11 per cent.   Use either the gravimetric process by direct solution, or fuse 2 grams of sample with 20 grams of sodium carbonate plus 4 grams of niter, and proceed as in sulphur in high silicon ferro-vanadium, filtering out the sodium titanate before acidulating with HCl.

Titanium in Steel.

Gravimetric.

The titanium is determined gravimetrically as in soluble ferro-titanium except that four or five grams of sample should be used.

VOLUMETRIC.

So far the most practical way is the well-known color method, using hydrogen peroxide. The author proceeds as follows:

Determine gravimetrically the amount of titanium in a ferro-titanium containing about 8 to 10 per cent of titanium.

PLAIN TITANIUM STEEL.

If the titanium content is 0.05 per cent or over, weigh 0.500 gm. of drillings into a 10 by 1 inch tube. Also weigh 0.500 gram of a plain carbon steel that contains no titanium by the qualitative test. Add to the latter enough of the standard ferro-titanium to bring the amount of titanium present in this standard mixture to within about 0.05 per cent of the titanium content of the test. If the test is likely to be about 0.15 per cent Ti, then the standard should either be about 0.10 per cent Ti or 0.20 per cent Ti. The nearer the standard is to the test, in titanium content, the better.

Dissolve the drillings in 10 c.c. of dilute sulphuric acid, 1 : 3; add 5 c.c. of conc. nitric acid and boil off red fumes. Cool; rinse the standard into a glass-stoppered comparison tube about 15–16 mm. outside diameter and with the graduated part about 38 cm. long. Add to the solution in the comparison tube 5 or 6 c.c. of the peroxide mixture used in qualitative Ti and V tests. Stopper the tube and mix the contents thoroughly. Transfer the test to the other comparison tube and treat it in like manner. If there is a great difference in color between standard and test, results will only be roughly approximate and the work should be repeated, preparing a new mixture of standard ferro-titanium and plain carbon steel, to imitate the test within the 0.05 limit or closer.

The following actual case will illustrate calculations, etc.:

The standard mixture consisted of 8 mg. of 8 per cent Ti ferro plus 500 mg. of a plain carbon steel of approximately the same carbon content as the sample to be tested.

The test matched the standard at 38.3 c.c. with the standard diluted to 35 c.c. Since the standard contained 8 mg. of 8 per cent ferro-titanium, its color was due to the presence of 0.008×0.08, or 0.00064 gram of metallic titanium; therefore we have the proportion:

Stand. Vol.   Test Vol.

$$35 \text{ cc.} \quad : \quad 38.3 \text{ c.c.} \quad : : \quad 0.00064 \quad : \quad X,$$

or $38.3 \times 0.00064 \div 35 = 0.0007$, or 0.0007, gram of titanium found. $0.0007 \times 100 \div 0.5 = 0.14$, or 0.14 per cent titanium when 0.5 gram is taken for analysis. The gravimetric result on this sample was 0.158. Another sample gave 0.134 per cent by color and 0.140 per cent by gravimetric analysis.

For percentages as low as 0.05 per cent and under, use a gram of sample and proceed accordingly, preparing standard mixtures of similar percentage. If the titanium steel also contains not over one-half per cent of elements that color acid solutions, such as chromium and nickel, the amounts of the latter present in the test should be determined by the rapid methods given under chromium and nickel in steel. Add to the standard enough shot nickel if titanium nickel steel is being tested, or enough potassium dichromate reduced with the least possible excess of sulphurous acid if the test be chrome-titanium steel, to exactly imitate the sample under examination, and then proceed as usual.

If the steel contain several per cents of chromium, fuse 2 grams with a mixture of 20 grams of sodium carbonate and 4 grams of niter. Dissolve the melt in water. Filter; wash the residue on the filter with sodium carbonate water.

Roast the pulp out and fuse again as before. Dissolve in water, filter and wash. Then dissolve the residue off the filter with hot hydrochloric acid. Wash the filter free of iron test. Dilute the filtrate and washings to 300 c.c. and pass H_2S through it until all platinum has been precipitated. Filter; wash the sulphides with H_2S water. Evaporate the filtrate and washings to 10 c.c., adding one gram of potassium chlorate before beginning the evaporation, to oxidize the iron and remove H_2S.

Add at this stage 30 c.c. 1 : 3 sulphuric acid and evaporate to heavy fumes. Dilute with water and then finish exactly as in the gravimetric determination of titanium in plain carbon steels.

The color method might also be applied to such steels by first removing the chromium by a sodium carbonate and niter fusion as just given, using 0.500 gram of sample. The sodium titanate and oxide of iron could then be spread, filter and all, in a small porcelain dish with 30 c.c. 1 : 1 hydrochloric acid and heated for 30 minutes or more. The pulp could be filtered out and washed; 30 c.c. of 1 : 3 sulphuric acid added; the filtrate and washings evaporated to thick fumes; transferred to a 10 by 1 inch test tube; boiled with 5 c.c. conc. nitric acid and finished by color. For a standard add to a plain chromium steel a suitable amount of ferro-titanium and fuse with sodium carbonate and niter, putting the fusion, etc., through exactly as the test. Use this for the color standard. Or after removal of the chromium and vanadium by a double fusion with sodium carbonate and niter, then fuse the iron oxide and sodium titanate with potassium bisulphate and finish by color, or gravimetrically.

Vanadium-Titanium Steel.

Remove the vanadium by fusion as in removal of chromium. Then finish gravimetrically as given under chro-

mium titanium steel, or convert into sulphate; evaporate to 10 c.c.; wash into a 10 by 1 inch test tube; boil with 5 c.c. conc. nitric acid, and finish by color.

QUALITATIVE TEST FOR TITANIUM.

Proceed as given under Qualitative Test for Vanadium, page 5.

ANALYSES.

Insoluble Ferro-Titanium.		Soluble Ferro-Titanium.	
	Per cent.		Per cent.
Titanium} Oxide }Ti₂O₃	87.80	Titanium............	8.12
		Manganese..........	0.58
Silica SiO₂..............	0.85	Silicon.............	0.50
Iron Oxide Fe₂O₃........	4.64	Iron................	86.92
Sulphur	0.52	Aluminum..........	3.00
Carbon................	1.89	Phosphorus	0.10
Phosphorus............	0.055	Carbon.............	0.26

CHAPTER IV.

ANALYSIS OF TUNGSTEN POWDER.

Fuse 0.6 gram of the powder with a mixture of 10 grams of carbonate of soda well ground in a mortar with 2 grams of potassium nitrate. A complete fusion is obtained in twenty minutes. The melt is dissolved with water in a platinum dish. It is transferred to a 300 c.c. casserole and acidulated with hydrochloric acid — keeping the dish covered during acidulation. The solution is heated for a half-hour with cover on, or until all danger of loss by spraying is over. The cover is removed and the acidulated fusion is evaporated to dryness. 10 c.c. of 1 : 1 hydrochloric acid are then added and the contents warmed until iron is dissolved. 200 c.c. of water are next put into the dish, and the solution is heated for thirty minutes to dissolve all sodium salts.

The precipitated tungstic acid is filtered out and washed free from iron test with very dilute hydrochloric acid. It is washed twenty more times to insure removal of salts. The filtrate and washings are again evaporated to dryness, dissolved, filtered, and washed as before. This second filtrate and washings are treated with a hydrochloric acid solution of cinchonine to remove the last traces of tungstic acid.

The three portions of the tungsten are burned off at a low red-heat until bright yellow. This yellow residue is weighed and fused with 10 grams of potassium bisulphate until the fusion is clear and transparent. The melt is

cooled and dissolved in a platinum or porcelain dish in a water solution of 15 grams of ammonium carbonate, warming gently to hasten solution. Remove the dish from the heater as soon as the fusion is dissolved.

The small residue of iron and silica is filtered out and washed free of sulphate test with ammonium carbonate solution. This residue is ignited and weighed, and its weight deducted from the weight of the yellow oxide. The remainder is multiplied by 79.31, and divided by the weight of sample taken for analysis to obtain the percentage of tungsten. If the silica residue is large or has yellowish tints, fuse it again. It may contain tungsten. Unless it is fused again, dissolved in ammonium carbonate and washed and weighed, the tungsten result will be too low. This last weight will be the correct deduction for silica, iron oxide, etc. If the first fusion and preceding operations have been conducted as given, the silica will be practically pure white, containing only traces of other oxides.

When the first bisulphate fusion is being dissolved in ammonium carbonate water, as stated, it should not be more than warmed to start the action, and the heat should be shut off the moment the bisulphate is in solution, otherwise tungsten may be found with the silica.

Rapid Method for Tungsten. Weigh one gram of metal into a platinum dish. Add 10 c.c. of pure hydrofluoric acid. Cover with a lid. Warm in a good draught. Remove from fire. Add three or four drops of concentrated nitric acid. Violent action occurs at this point. Continue to add nitric acid a drop at a time until further additions of acid produce no action. This will take, in all, about 5 c.c. of conc. nitric acid. Remove the lid, rinsing off its surface, permitting the washings to flow into it. Add 10 c.c. concentrated sulphuric acid. Evaporate to thick fumes of SO_3. Cool, moisten with 10 c.c. of conc.

hydrochloric acid. Add 10 c.c. of water, transfer the contents of the dish to a 600 c.c. casserole, and heat to boiling with constant stirring to prevent bumping. Cool. Filter. Wash with 1:10 hydrochloric acid until free of iron test. Ignite and weigh the tungstic acid as trioxide. Fuse the latter with potassium bisulphate and finish as in the first method. This rapid scheme is a modification of Arnold & Ibbotson's method, and usually gives results one or two tenths of one per cent lower than the longer method, which must be resorted to for complete analysis of the powders. See Arnold & Ibbotson's "Steel Works Analysis," 1907.

Iron, Phosphorus, and Sulphur. If these elements are asked for, 1 gram of sample should be fused with 20 grams of sodium carbonate and 4 grams of potassium nitrate. Then proceed exactly as for tungsten until just before adding the cinchonine. (A) Divide the filtrate and washings, instead of adding the cinchonine, into two equal parts. To one portion add the cinchonine, the small precipitate is burned off and weighed by itself. Evaporate it with a little hydrofluoric and sulphuric acids. Ignite it and multiply its weight by two. Add this amount to the tungsten trioxide found by the two evaporations to dryness. Calculate this total trioxide to percentage on the basis of one gram taken for analysis. (B) To the other portion of the divided filtrate and washings obtained after the second evaporation, add a slight excess of ammonia. Heat, filter, and wash with hot water. Ignite this precipitate, but do not weigh it, as it is almost sure to contain nearly all of the tungsten that remained in this portion of the divided filtrates. Dissolve it with hydrochloric acid; evaporate off excess of acid; dilute with water; filter out any tungstic acid that may separate, washing the latter free from iron with 1:20 hydrochloric acid. The filtrate and washings are evaporated to thick fumes

with 60 c.c. 1:3 sulphuric acid and reduced with zinc and titrated with the same permanganate standard that is used for iron oxide determinations in graphite (see page 187). Calculate the iron found as metal, and multiply the result by two to obtain the percentage on the basis of one gram.

Phosphorus. (When phosphorus and sulphur are sought, obtain the iron from a separate fusion.) Starting at (B) add enough ferric chloride solution free from phosphorus and sulphur to color the "other portion of the divided filtrate" a distinct yellow unless the powder, or ferro, already contains considerable iron. Add a small excess of ammonia to the hot, slightly acid filtrate. Heat; filter and wash the iron hydroxide with water. Dissolve it off the filter with hot 1:1 hydrochloric acid. Wash the filter free of iron. Evaporate this filtrate and washings to a few c.c. on the water bath. Filter out the tungstic acid that nearly always appears. Evaporate filtrate and washings again to a few c.c. Add 50 c.c. of concentrated nitric acid and evaporate to about 5 or 10 c.c. Add 25 c.c. of concentrated nitric acid and once more reduce the volume. Add 25 c.c. water, and filter, if not clear, washing with the dilute nitric wash used in phosphorus in steels. Evaporate the filtrate and washings to 40 c.c. Boil with a moderate excess of permanganate solution, and finish as in steels.

Sulphur. The first filtrate and washings obtained from the ammonia precipitation of the iron are made slightly acid with hydrochloric acid. Barium chloride is added, and the sulphur is finished as in gravimetric sulphur in steels. Multiply the result by two to bring it to one gram taken for analysis.

When sulphur is determined, a blank should be run, beginning with the melting of the same flux. The BaSO₄ obtained is deducted before calculating the per cent of sulphur.

Carbon. Burn three grams with four grams of red lead, deducting the blank due to the lead.

Manganese. Fuse 0.100 gram with 2 grams sodium carbonate and 0.5 gram of niter. Remove tungsten by one evaporation to dryness. Dissolve in 5 c.c. 1 : 1 hydrochloric acid; filter; wash; evaporate to fumes with 10 c.c. 1 : 3 sulphuric acid. Dissolve in 10 c.c. of water; wash into a 10 by 1 inch tube; dilute to 20 c.c. with water. Add 10 c.c. concentrated nitric and finish as in steels. Accurate to 2 per cent if 0.050 gram are taken for analysis when the manganese exceeds 1 per cent.

For higher per cents of manganese fuse 1 gram and remove tungsten by one evaporation. Convert the filtrate into sulphate; rinse it into a liter flask and proceed as given for high manganese in ferro-titanium.

Molybdenum in Tungsten Powders. Fuse one gram as for tungsten. Dissolve the melt in as little water as possible. Filter. Wash with sodium carbonate water. Add to the filtrate and washings four grams of tartaric acid. Then make the filtrate very slightly acid with hydrochloric acid. Warm. Pass H_2S for an hour, or until the brown sulphide settles well. Filter off the sulphide. Wash it thoroughly with H_2S water. Ignite the precipitate at a very low heat until white or bluish white. If it looks yellow, fuse it with a little sodium carbonate; dissolve the melt in water; add a crystal of tartaric acid and proceed as before with H_2S.

When the bluish-white molybdenum trioxide is obtained, multiply its weight by 0.6666 after deducting the silica, etc. See Molybdenum in Steel. The methods given for tungsten powder apply also to ferro tungsten.

CHAPTER IV

Part II.

TUNGSTEN, SULPHUR, SILICON, MANGANESE, AND PHOSPHORUS IN TUNGSTEN STEEL AND CHROME TUNGSTEN STEEL.

(First Method for Tungsten in Steel.) *

I<small>F</small> the sample contains considerable chromium and tungsten, proceed as follows: Weigh $1\frac{1}{2}$ to 2 grams of drillings (see Annealing of Steel, page 195) into a No. 5 Royal Berlin porcelain evaporating dish. Add slowly to the drillings, keeping the dish covered with watch glass, a mixture of 30 c.c. conc. hydrochloric acid (1.20 specific gravity) and 30 c.c. conc. nitric acid. Mix the two acids thoroughly before applying them to the steel if phosphorus is wanted. Heat until action ceases, and if the residue in the bottom of the dish is not bright yellow, repeat the addition of acid and continue to heat the dish until tungsten residue is a clean yellow. Then remove the cover and evaporate the contents of the No. 5 dish to 15 c.c. Keep the heat low enough to prevent spattering. Do the evaporating on a graphite or sand bath. A six-inch pudding pan filled two-thirds full of graphite heated by an ordinary Bunsen burner makes a simple contrivance for the evaporations. The pan can be set on a tripod or an earthenware flame guard with the burner directly under the center of the pan. With such an arrangement, a flame an inch long will furnish sufficient heat. The guard

* See also page 74.

answers the twofold purpose of supporting the pan and
shielding the flame from currents of air. The earthenware
has the additional advantage of being acid proof. Add 50
c.c. conc. nitric acid. Put the watch glass on the dish and
heat till action ceases. Remove the cover and evaporate
to 15 c.c. Again add 50 c.c. conc. nitric acid and evap-
orate to hard dryness. Ignite the dish and its contents
to a dull red, raising the heat *slowly* to prevent cracking.
Set the dish over a bare flame for this purpose. The terra
cotta flame guard, with the pan removed, answers quite
well for a support during the ignition. Lower the flame
slowly and set the dish on a warm place, cooling it gradually.
When the dish is just warm, pour into it 50 c.c. of conc.
hydrochloric acid. Put the cover on and heat to slow
boiling. Continue to boil until the residue in the bottom
of the dish is bright yellow. Then remove lid and
evaporate to 15 c.c. Cool, and add 30 c.c. distilled water
and ashless paper pulp. Filter on a double 11 cm. ashless
filter (a double filter will run faster than a single one); wash
with 1 : 20 hydrochloric acid until the washings give no
test for iron with potassium or ammonium sulphocyanate.
Return the filtrate and washings to the No. 5 dish for
concentration.

Roast the paper out of the residue of tungstic and silicic
acids in a weighed 20 c.c. platinum crucible. Do not heat
tungstic acid to a bright red, as it slowly sublimes at high
temperature. When the ash is bright yellow, free from
black, cool in a desiccator and weigh. This weight will
consist of mainly tungstic acid and silica contaminated
with a small quantity of oxides of iron, and chromium,
also, if the latter element be present. Add three drops of
1 : 3 sulphuric acid to the residue, and fill the crucible two-
thirds full with c.p. hydrofluoric acid. Evaporate in a
good draft to moist dryness. Drive off the sulphuric acid
by heating the crucible near the top. When all heavy

fumes are gone, heat to low red and weight as $WO_3 + Fe_2O_3 + Cr_2O_3$. The difference between this weight and the first weight is the silica which has been volatilized. This loss of weight multiplied by 47.02 and divided by the weight of sample taken, equals the per cent silicon present in the steel. In the meantime the filtrate and washings from the first filtration should be evaporating until a slight ring of basic iron forms around the margin of the fluid. This ring dissolves rather slowly when the dish is rocked backwards and forwards. In other words, leave only enough acid to keep the iron in solution. (However, care must be taken not to overdo the removal of the excess of acid, as basic iron may separate in the solution when it is heated for the precipitation of phosphorus.) Add 20 c.c. of water; filter through a 9 cm. ashless filter into a 150 c.c. beaker. Wash the residue on the filter until all yellow color due to chloride of iron is gone. About 15 washings should suffice. Wash every other time with 1 : 20 hydrochloric acid. If the volume of the filtrate and washings is over 50 c.c. reduce it to that amount by evaporation. Heat to boiling, remove from fire, precipitate with molybdate solution, and finish the phosphorus as in steels. The residue obtained from the second evaporation of original filtrate from the tungstic acid, etc., after being washed free of color of iron chloride, is further washed free of iron test and burned off in the same platinum crucible with the residue from which the silica was removed by hydrofluoric acid. This total residue which constitutes the tungsten plus small quantities of iron and chromium oxides is weighed again. If the original tungstic acid was thoroughly clean and yellow before the first evaporation to 15 c.c., then the amount of chromium oxide is negligible.

The $WO_3 + Fe_2O_3 + Cr_2O_3$ residue is fused with five grams of carbonate of soda. The melt is dissolved with hot water. The small residue of iron is filtered out and

washed free of carbonate. It is burned to a red flake in the same crucible, which meanwhile has been thoroughly rinsed free of carbonate with distilled water. The residue is weighed and its weight deducted from the weight of the $WO_3 + Fe_2O_3 + Cr_2O_3$.

If the filtrate from the carbonate fusion is quite yellow, make it acid with sulphuric acid, boil with a slight excess of permanganate, and determine the chromium as in steels. Calculate the milligrams of chromium found to chromic oxide, and deduct it from the $WO_3 + C_2O_3$. The remainder is the tungsten oxide, which multiplied by 79.31 and divided by the weight taken for analysis gives the percentage of tungsten. If the filtrate from the sodium carbonate fusion is only slightly yellow, the chromium may be ignored in the calculations.

(A) An excellent way to remove oxides of silicon, iron, and chromium from the tungstic oxide is to fuse with five grams of potassium bisulphate. This fusion can be made quickly. Heat the crucible at first to a very low heat, below redness, until the bisulphate is molten and slight fumes of sulphuric anhydride appear. Then raise the heat carefully to low redness. Keep the lid on the crucible, raising it only slightly to observe the progress of the fusion. When redness has been reached and all danger of spattering is over, raise the lid, and if the contents of the crucible are in a state of transparent fusion, with no yellow specks left undissolved, the fusion is completed. One can see the bottom of the crucible through the transparent molten mass, and, if only pure white flakes of silicic acid are floating about, the melt is perfect. Cool. Dissolve in 10 grams of ammonium carbonate and 100 c.c. of water, placing the crucible in the ammonium carbonate solution contained in a small casserole. Warm the casserole slightly to hasten matters. Keep it covered with a watch glass to prevent loss during heating. (Use a casserole

if a platinum dish cannot be had.) Filter, adding a little paper pulp. Wash with water containing ammonium carbonate until the washings are no longer milky when acidulated with a few drops of hydrochloric acid and tested with barium chloride. Then wash 10 times more. Ignite and weigh in the same crucible, and deduct the residue, which consists of all of the SiO_2, Cr_2O_3, and Fe_2O_3, from the WO_3, etc., and calculate to percentage. The residue of SiO_2, if not pure white, is evaporated with hydrofluoric and sulphuric acid in the usual way, and the loss of weight constitutes the silicon present in the steel when multiplied by 47.02 and divided by the weight taken for analysis.

The *sulphur* in such steels should be obtained by fusing 2 grams of thin drillings with 20 grams of sodium carbonate and five grams of potassium nitrate. Dissolve in water, filter, wash, roast, fuse again, acidulate with HCl, evaporate to dryness twice, filter after each evaporation, washing with 1 : 20 HCl; precipitate the filtrate with barium chloride and finish as in gravimetric sulphur in steels. Make blank determination on like amount of the flux and acids, proceeding exactly as in actual analysis, and deduct the sulphur found from that found in the fusion of the steel. Multiply the weight of barium sulphate less that found in the blank by 13.73, and divide by the weight of sample taken for analysis to obtain the per cent of sulphur. The sulphur can also be obtained by direct solution in nitric acid, in all steels that will dissolve in it. Finish as in plain steel.

Manganese. Proceed as for manganese in steel when chromium is *present*, digesting the sample thoroughly with the mixture of acids as given, but omit the use of zinc oxide unless chromium be found.

CHAPTER IV.

Part III.

ANALYSIS OF LOW PER CENT TUNGSTEN STEELS.

When tungsten, phosphorus, and silicon are wanted in steels that contain 3.0 to 3.5 per cent tungsten and less than 1 per cent chromium, dissolve 3 grams in 60 c.c. of 1.20 nitric acid, in a No. 5 dish. Evaporate to dryness. Ignite to dull red. Cool and dissolve in concentrated hydrochloric acid, and finish as given under the analysis of high chromium-tungsten steels when silicon and phosphorus are wanted.

Analysis of All Tungsten and Chrome Steels when Chromium and Tungsten, only, are asked for.

(Third Method for Tungsten in Steel.)

Dissolve two grams of sample in 30 c.c. 1:3 sulphuric acid. Heat until all action is over. Add 60 c.c. 1.20 nitric acid and digest at just below boiling until the residue in the 400 c.c. beaker is a clear yellow free of black particles. Dilute to 200 c.c. with water, and boil for 20 minutes. Add some paper pulp, filter, and wash free of iron test with dilute sulphuric acid. Dilute the filtrate to 500 c.c. and mix. From this solution fill a 250 c.c. flask to the mark.

First Portion. Precipitate the remaining tungstic acid from this portion with cinchonine. Wash it free of iron test with water containing cinchonine solution. Ignite

it. Weigh and fuse with twenty times its weight of bisulphate of potassium. Obtain the amount of pure WO_3 as given under bisulphate fusion in A. See page 62. Multiply the weight of WO_3 by 2. Iron can also be removed by sodium carbonate fusion. See page 61. The main tungsten precipitate is ignited, weighed and purified in the same manner. The weight of WO_3 thus obtained is added to twice the weight of the WO_3 obtained by the cinchonine. This sum is multiplied by 79.31 and divided by the weight taken for analysis to obtain per cent of tungsten.

Second Portion. Finish this for chromium as given under determination of chromium in chromium-vanadium steel, pages 8 and 32. If the chemist prefers to obtain the chromium by a separate analysis, he can get the total tungsten by one operation. The entire filtrate from the main tungsten residue is precipitated without dividing it, by cinchonine. This precipitate is burned off with the main residue. The combined residues which constitute the total tungsten from two grams of sample are then freed from impurities in the usual way with bisulphate or sodium carbonate, and the total weight of pure WO_3 is multiplied by 79.31 and divided by the weight taken for analysis to obtain the per cent of tungsten. If the iron oxide is removed by sodium carbonate the silica is first removed by evaporation with hydrofluoric acid and sulphuric acid as given on page 60. The oxides are ignited, weighed, and then the iron is removed by the carbonate fusion.

Cinchonine Solution.

Dissolve 25 grams of cinchonine in 200 c.c. of 1 : 1 hydrochloric acid.

Cinchonine precipitates tungsten almost instantly from hydrochloric solution. It precipitates molybdenum after

considerable lapse of time, and then only partially.   At
least, the above statement regarding molybdenum is cor-
rect if the attempt is made in the manner as given for
tungsten.   This constitutes a distinct difference between
these two elements.

ANALYSIS OF CHROME-TUNGSTEN-VANADIUM STEELS FOR CHROMIUM AND VANADIUM.

These elements are determined as in chrome-vanadium
steels, boiling with sufficient excess of permanganate so
that the tungsten residue looks brown from manganese
oxide after twenty minutes' boiling.   Filter on asbestos
and finish as usual.   See pages 8 and 32.

CHAPTER V.

MOLYBDENUM POWDERS.

Carbon.

Carbon is obtained by direct combustion in a stream of oxygen, using the electric furnace with temperature between 900 and 950 degrees Centigrade. Decarbonization takes about a half-hour. Use some red lead when the silicon content is high; two grams of the former per gram of Mo.

Phosphorus.

Phosphorus is obtained by heating 1.63 grams of the powder in 30 c.c. of 1.20 nitric acid until red fumes are gone. Boil with an excess of potassium permanganate solution. Stir the contents of the beaker during the boiling to prevent bumping, due to the large quantity of molybdic acid which separates. Add a slight excess of ferrous sulphate and boil for another five minutes. Filter out the molybdic acid; wash it with dilute nitric wash. Finish the filtrate for phosphorus as in steels. If the phospho-molybdate adheres to the beaker, instead of stirring easily through the solution, it is contaminated with molybdic acid. For such powders use 0.815 gram for analysis, and proceed in the same manner as just given for 1.63 grams of sample.

Silicon.

Dissolve 1.5 grams in 60 c.c. 1.20 nitric acid. Add 120 c.c. of 1 : 3 sulphuric acid. Evaporate in a porcelain dish on graphite or sand bath to thick white fumes of sulphuric

anhydride. Cool and add 80 c.c. 1 : 1 hydrochloric acid.
Boil five minutes. Cool again and add 50 c.c. of water.
Mix in some paper pulp and filter on an 11 cm. double
ashless filter. Wash free from iron test with 1 : 10 hydro-
chloric acid. Then wash free from chloride test with dis-
tilled water. Ignite in a platinum crucible at the faintest
red-heat until white. Weigh and evaporate with hydro-
fluoric acid and a few drops of sulphuric acid. Ignite
again at lowest visible redness. Calculate the loss of
weight as usual to silicon.

MOLYBDENUM.

First Method.

Fuse 0.500 gram of finely ground powder with twenty
times its weight of sodium carbonate plus two grams of
potassium nitrate. Heat cautiously until the fusion is free
from black particles. Dissolve the melt in a platinum or
porcelain dish (platinum preferred) with water. Remove
the platinum crucible from the dish and rinse it off carefully,
allowing the washings to run on the filter through which
the water solution is to be poured. Mix the water solution
of the fusion with a little paper pulp and filter it through
the filter aforesaid. Wash the residue forty times with
dilute sodium carbonate water. The residue on the filter
contains all of the iron and copper present in the metal, a
little platinum oxide from the crucible, and a little molyb-
denum.

The filtrate and washings are transferred to an 800 c.c.
beaker. Two grams of tartaric acid are added. The
solution is acidulated with sulphuric acid in *slight* excess.
The acidulated solution is heated for twenty minutes to
expel the major portion of the carbon dioxide. It is then
cooled; three drops of phenolphthaleine solution are added.
(See Phosphorus in Steel, p. 163.) A rather concentrated

solution of sodium hydroxide is added until one drop produces a pink color. Next add 1 : 3 sulphuric acid until one drop causes the solution to become colorless. Dilute to 700 c.c. with water. If the attempt be made to precipitate molybdenum, in too acid a solution, by the hydrogen sulphide, the former is partially reduced to a blue oxide and partially precipitated as sulphide. To avoid this highly undesirable condition it is merely necessary to keep the solution but very slightly acid until it is well saturated with H_2S. It then turns to a deep orange-colored fluid from which the molybdenum is quickly precipitated, by the addition of six or seven c.c. of 1 : 3 sulphuric acid, as a brown sulphide. Pass the gas for thirty minutes longer. Add paper pulp to the beaker, mixing it well with the sulphide just before passing the gas for the half-hour as directed. In this way the precipitation is rapid. The sulphide can be filtered and washed quickly. It is washed with H_2S water containing two drops of 1 : 3 sulphuric acid per 500 c.c. of wash water. Give the sulphide forty washings, permitting each washing to drain off thoroughly before the succeeding one is applied. The sulphide is then roasted just below redness in a platinum crucible. The contents of the crucible can be ignited without loss of molybdenum trioxide, but the crucible must not be allowed to exceed the faintest visible redness. The MoO_3 usually burns to a brownish-white residue, owing to traces of impurities.

After weighing the oxide it is extracted with 1 : 1 ammonia (11.50 per cent) on the water bath until there remains but a small residue, consisting of traces of iron and some silica. This is mixed with a little paper pulp, filtered, washed thoroughly with dilute ammonia water.* It is

* If this filtrate and washings are blue estimate the copper therein with KCN as in steels, page 89; calculate the copper found to CuO and deduct the result from the weight of the impure MO_3.

ignited, weighed, and its weight is deducted from the first
weight of the MoO_3. The remainder is multiplied by
66.66 (or $\frac{2}{3} \times 100$), and divided by the weight taken for
analysis to obtain the per cent of molybdenum in the
sample. The filtrate and washings from the sulphide
precipitation should always be tested by passing H_2S
through it for an hour more to make sure that no further
precipitation of molybdenum sulphide will occur. If
the directions as given are carefully followed, no molyb-
denum will be found at this point.

Second Method.

Completely soluble molybdenum can be examined for
molybdenum as follows: Dissolve 0.400 gram of fine
ground sample in 30 c.c. of 1.20 nitric acid. Cool and
add two grams of tartaric acid. Then add an excess
of ammonia. Drop in 1:3 sulphuric acid until the
solution is just faintly acid. Dilute to 800 c.c.; pre-
cipitate with hydrogen sulphide and finish for molyb-
denum as given in the first method.

Iron.

The residue of iron, etc., remaining on the filter from
the water solution of the sodium carbonate and niter fusion
is dissolved off with a little hot 1:1 hydrochloric acid.
The filter is washed free from iron test. This filtrate and
washings are almost certain to contain some molybdenum.
(The writer has found molybdenum with the iron, even
after it has been fused a second time with sodium carbon-
ate.) Add dilute ammonia to the solution a drop at a time
until the iron hydroxide appears. Then add sulphuric
acid (1:3) until the iron precipitate just dissolves. Dilute
to 300 c.c. with water. Pass H_2S. The small quantity
of molybdenum quickly separates. It is filtered out and

washed in the same manner as the main sulphide precipitate. Ignite this sulphide to oxide, weigh it, extract it with ammonia in the same way as the main oxide. Filter out the insoluble matter, and wash it with dilute ammonia. Ignite it, weigh it, and deduct the weight from the first weight; calculate the remainder to Mo, and add it to the principal part of the molybdenum found. The filtrate and washings from the small sulphide precipitate contain all of the iron which can be determined by evaporation to a small volume with a slight excess of potassium chlorate. One or two grams should suffice. Then add an excess of 1:3 sulphuric acid and evaporate to thick white fumes of sulphuric anhydride. Dilute with water. Reduce with zinc oxide or metallic aluminum, and finish by titration with permanganate solution as in the determination of iron in ferro-vanadium. See page 30.

Tungsten.

Evaporate the filtrate and washings from the main sulphide precipitate obtained by the first method to moist dryness. Add 100 c.c. of conc. nitric acid. Heat with cover on until all action is over. Remove the watch glass from the casserole and evaporate again to moist dryness. Add water; heat until all salt is in solution; filter out the insoluble residue; wash it free from salts with 1:20 hydrochloric acid. This will take about forty to fifty washings. Evaporate the filtrate and washings again to moist dryness, and add 100 c.c. of conc. hydrochloric acid. Heat with the cover on as before, and evaporate a third time. Add water; heat; filter; wash with 1:20 hydrochloric acid, and add the washed residue to the first one obtained after evaporating with nitric acid. Ignite and weigh as $WO_3 + SiO_2$. Finish as given for tungsten in steels.

SULPHUR.

Fuse 2 grams with 20 grams of sodium carbonate and 4 grams of potassium nitrate. The fluxes are ground thoroughly together in an agate mortar. Heat until the melt is a clear light yellow, free of black specks. This requires but a few minutes. Dissolve the melt in water. Transfer it to a casserole. Acidulate with concentrated hydrochloric acid, and evaporate to dryness on the water bath. Add 10 c.c. of 1:1 hydrochloric acid. Heat with the cover on for a half-hour. Add water and heat again. Filter and wash with 1:20 hydrochloric acid, forty times. Heat the filtrate to boiling, and precipitate with barium chloride solution, adding the latter in excess, about 50 c.c. of the saturated solution. Considerable molybdenum is precipitated with the barium sulphate. Filter, washing with water, only, until free from chloride test to insure removal of the excess of $BaCl_2$. Plug the end of the funnel with a rubber cap and fill it three-fourths full with 1:1 ammonia water (11.50 per cent) and keep covered four hours, or longer if convenient. Then allow this fluid to drain off, and wash the residue with the 1:1 ammonia until 10 c.c. of the washings on being acidulated in a 254 by 25.4 mm. tube with hydrochloric acid, brought just to a boil with granulated tin (Do not continue to boil. See qualitative Mo test, page 2), cooled to room temperature and treated with one or two c.c. of KCNS solution, give no reddish coloration due to molybdenum. Ignite and weigh as $BaSO_4$ as in steels. Deduct a blank. It is always safer to fuse this $BaSO_4$ with sodium carbonate; dissolve the fusion in water; filter it; acidulate it with hydrochloric acid, and reprecipitate it with barium chloride as described under gravimetric sulphur in steels, page 177.

Manganese.

Proceed as in steels or ferro-vanadium, dissolving the powder in 1.20 nitric acid.

Copper.

Nitric acid solutions of molybdenum are precipitated but slightly, even after one hour's standing, by potassium-ferricyanide. This reagent affords a rapid means of determining the amount of copper that may be present in the molybdenum. Dissolve 1 gram of sample in 30 c.c. 1.20 nitric acid. Add ammonia until the iron hydroxide forms. Then add sulphuric acid (1:3) a few drops at a time until the hydrate of iron is just dissolved. Now precipitate the copper with 20 c.c. of the same potassium ferricyanide solution used to separate copper in ferro-vanadium. See page 94. If the copper in solution is likely to exceed ten milligrams, then add an additional 2 c.c. of the ferricyanide solution for every milligram of copper in excess of ten milligrams. Finish as given in the author's method for copper in steel, page 89. The analysis of ferro-molybdenum is similar to that of the powders.

TYPICAL ANALYSES.

		Carbonless.
	Per cent.	Per cent.
Carbon.................................	4.60	0.07
Manganese.............................	0.03	0.18
Phosphorus............................	0.029	0.059
Sulphur...............................	1.02	....
Silicon...............................	0.50	2.88
Molybdenum............................	90.00	92.50

CHAPTER V.

PART II.

METHOD FOR TUNGSTEN AND MOLYBDENUM STEELS.

ABSENCE OF MOLYBDENUM.

(*Second Method for Tungsten in Steel.*)

DISSOLVE 2 grams of steel in a mixture of 30 c.c. of concentrated nitric acid and 30 c.c. of 1.20 specific gravity hydrochloric acid in a No. 5 porcelain dish. Keep at a digesting heat until the tungstic acid is a bright yellow. Agitate the solution frequently by stirring the sediment vigorously, but do not leave glass rods in the hot acid. Remove the former after each stirring, as tungstic acid attacks glass in hot acid solution, causing silicon results to be too high. When the tungstic acid is a clear yellow remove the lid and evaporate to 20 c.c. volume. Now add 100 c.c. of distilled water. Stir thoroughly. Remove stirring rod. Heat to incipient boiling for at least a half-hour. Filter, adding ashless paper pulp. Wash with 1 : 20 hydrochloric acid until free of iron test. Ignite and weigh as $WO_3 + SiO_2 + Fe_2O_3$. Evaporate with hydrofluoric and sulphuric acids as described on page 60. Weigh as $WO_3 + Fe_2O_3$. The loss of weight here is part of the total silicon. This is the most rapid of the three methods for tungsten in steel.

Fuse the $WO_3 + Fe_2O_3$ with five grams of sodium carbonate until molten. Keep molten for 20 minutes. Dissolve in a casserole with distilled water. Filter out the small residue of iron and wash it with water until free of carbonate. About forty washings will suffice. Ignite this residue in a weighed crucible, and deduct its weight

from the weight of $WO_3 + Fe_2O_3$. The remainder is the pure WO_3, which, multiplied by 79.31 and divided by the weight taken for analysis, yields the per cent of tungsten.

Silicon and Phosphorus.

If silicon and phosphorus are asked for, evaporate the filtrate and washings from the tungstic acid to 10 c.c. Add 50 c.c. conc. nitric acid and evaporate again to 10 c.c. Add 50 c.c. more of conc. nitric acid and evaporate to hard dryness. Ignite to dull red, and proceed as given on page 59 for the *balance* of the silicon and for the phosphorus.

In the Presence of Molybdenum.

Proceed as in the absence of molybdenum to the point where the filtrate and washings from the tungstic acid have been obtained. Transfer the fluid to a 500 c.c. flask. Dilute to the mark with water. Mix thoroughly, and from this, quantitatively fill a 250 c.c. flask.

Finish one portion for phosphorus and silicon as given in the absence of molybdenum. Calculate the phosphorus on the basis of one-half the original weight taken for analysis, that is, as though one gram were taken. The silicon obtained from this portion is multiplied by two and added to that obtained from the tungstic oxide. The total is calculated on a two-gram basis.

The tungstic oxide, which always contains a little, and sometimes much, molybdic oxide, is ignited at the faintest red-heat till yellow; weighed; the silica is removed from it by evaporating with hydrofluoric and a little sulphuric acid. The residue is then ignited at lowest possible heat and weighed again. The loss of weight at this point is the silica that remained with the tungstic oxide.

The remainder is the WO_3 plus some MoO_3 and Fe_2O_3. The combined oxides are fused with ten grams of sodium carbonate for a half-hour at a red-heat with a Bunsen

burner. The melt is dissolved in water; the iron filtered out and washed with water. It is ignited; weighed; and the weight is deducted. The filtrate and washings are treated with two grams of tartaric acid; are acidulated very slightly with sulphuric acid; and the molybdenum is separated with H_2S. The MoS_3 is ignited to oxide, and the weight of the oxide is deducted from the weight of $WO_3 + MoO_3$. The remainder is multiplied by **79.31** and divided by the weight taken for analysis to obtain the percentage of tungsten. See the directions for the precipitation of molybdenum as sulphide, given on page 69.

As molybdic oxide sublimes at a bright red-heat, hence the repeated caution not to ignite either it or the sulphide above the faintest suggestion of redness. A slight white fume rising in the crucible when heating the oxide, at redness indicates loss of the latter. The MoO_3 found with the tungstic oxide is calculated to Mo multiplying by 0.6666. This amount is added to twice the weight of Mo, in parts of a gram, found in the second 250 c.c. portion. The total is multiplied by 100 and divided by 2 to obtain the total per cent of molybdenum in the two-gram sample.

The principal part of the molybdenum, obtained in the second half of the divided filtrate, is separated as follows: Add ammonia to it until a precipitate forms that no longer dissolves on stirring. Add 1 : 3 sulphuric acid until this precipitate *just* dissolves. Then saturate the *nearly neutral* solution with hydrogen sulphide, and obtain the molybdenum in this half of the divided filtrate. If the solution containing the molybdenum is too nearly neutral, H_2S causes only a deep red coloration in it; if the solution is too acid, the passage of the hydrogen sulphide results in a partial precipitation of the molybdenum together with a blue coloration. From the red solution, the molybdenum is easily precipitated by a *very slight* addition of acid. Add

the latter cautiously, a c.c. or two at a time, until the molybdenum begins to settle rapidly. Then pass H_2S a little while longer. If the H_2S has been passed through too acid a solution of molybdenum, with the resulting partial precipitation giving a blue filtrate, the best thing to do is to begin the analysis over, giving proper attention to these details. The molybdenum can be completely precipitated, if the conditions are observed as here given, in a half-hour's time with a rapid stream of H_2S.

Volumetric Determination of Molybdenum in Steel.

After weighing the molybdenum as oxide, the results so obtained can be checked as follows: Fuse the oxide with 5 grams of carbonate of soda. Dissolve the melt in about 50 c.c. of water in a dish. Filter the solution on a 7 cm. filter. Wash the latter thoroughly with sodium carbonate water. Evaporate the filtrate and washings to 50 c.c. Acidulate with 1:3 sulphuric acid, adding an excess of 100 c.c. Next add 1 c.c. of 1:1 hydrochloric acid after acidulation with sulphuric acid.

Place in the beaker a square inch of 1.7 mm. ($\frac{1}{16}$ inch thick) aluminum foil with its corners bent at right angles. Heat the solution so as to maintain rapid action between the foil and the acid. In a half-hour the reduction is *usually* complete.

Titrate with potassium permanganate standard until three drops of the latter render the solution a distinct pink, in the cold, for one minute. Remove the foil before beginning the titration, rinsing it with cold water. Heat a similar piece of foil for a half-hour in a solution containing 5 grams of sodium carbonate acidulated with 120 c.c. 1:3 sulphuric acid. Add also 1 c.c. of 1:1 hydrochloric acid after acidulating with sulphuric acid. Titrate the blank exactly as given for the test. Deduct the c.c. of perman-

ganate used by the blank from the amount required to oxidize the test, and multiply the remainder by 0.001925 to obtain the weight of molybdenum present in the sample. The permanganate standard is prepared by dissolving 1.86 grams of the salt in water and diluting the solution to one liter. Its value in metallic iron multiplied by 0.88163 equals its value in MoO_3. This method possesses no advantage over the ignition of the sulphide to oxide and weighing as such.

WEIGHING OF THE MOLYBDENUM AS LEAD MOLYBDATE.

After weighing as oxide, fuse the latter with 5 grams of sodium carbonate. Dissolve the melt in water. Filter it, washing thoroughly with sodium carbonate water. To the filtrate and washings add two or three drops of methyl orange. Now titrate the solution until it turns pink with 1:1 HCl. Add 1 c.c. in excess. Heat the solution to almost boiling. Add 30 c.c of a filtered saturated solution of lead acetate in this manner: First add 20 c.c. and permit the precipitate to settle somewhat; then pour in the remaining 10 c.c., noting if there seems to be a further formation of the white precipitate. If more forms, add an additional 10 c.c., or 40 c.c. in all. Now add 50 c.c. of a solution of ammonium acetate.* Stir the mixture thoroughly, and allow the lead molybdate to settle for two hours. It is filtered, washed with hot water, and ignited at a low red-heat until white. It is weighed and the weight multiplied by 0.2616 to reduce the weight to gram of molybdenum. Test the filtrate and washings with 10 c.c. of the lead acetate solution, and note if a further precipitation occurs in the course of an hour or two. This is a satisfactory method, as a check. The ammonium acetate solution is prepared by dissolving 500 grams of the crystals in 1000 c.c. of water.

* Brearley and Ibbotson suggested the use of ammonium acetate at this stage.

CHAPTER VI.

ANALYSIS OF FERRO-CHROME, CHROME ORE, AND CARBONLESS CHROME.

FERRO–CHROME and carbonless chrome usually dissolve completely in 1 : 3 sulphuric acid. The ferro should be ground as fine as possible. Carbonless chrome dissolves readily without grinding to any especial degree.

When a residue of a gritty or metallic nature remains after digestion with the dilute acid, it is filtered out, washed twenty times with 1 : 10 sulphuric acid, roasted, fused with twenty times its weight of sodium carbonate plus a fifth of its weight of potass. nitrate. The fusion is dissolved in water in a platinum dish, or porcelain one, and then poured into the main solution.

Dissolve 0.3 to 0.4 gram of sample in 30 c.c. 1 : 3 sulphuric acid as described, fusing the residue if there be any. Add 60 c.c. 1.20 nitric acid, and treat exactly as stated for determination of vanadium in ferro-vanadium until the filtering through asbestos to remove the excess of manganese oxide has been accomplished. To the cold filtrate add 1 to 2 c.c. of the ferricyanide indicator. Add also 50 c.c. of 1 : 3 sulphuric acid. Titrate at once with a standard solution of ferrous ammonium sulphate of double the strength of that used for vanadium work. When three drops of this standard produce a darkening of the green to a blue, after the entire disappearance of all red or yellow tints, the end point is reached.

STANDARDIZATION AND CALCULATIONS.

Dissolve 39.163 grams of ferrous ammonium sulphate in
water; add 50 c.c. of 1:3 sulphuric acid; and dilute to one
liter for standard.   To standardize the ferrous ammonium
sulphate weigh into a 5-ounce beaker 0.500 gram of recrys-
tallized c.p. potassium dichromate.   Dissolve these crystals
in a small quantity of water.   Add to the water solution
sulphurous acid until the chromate is entirely reduced to
a dark green and smells distinctly of SO_2.   Then transfer
this green solution to a 600 c.c. beaker containing about as
much steel, free from chromium, as there is supposed to
be iron in the ferro-chromium.   For example, if the ferro
is supposed to contain 60 per cent chromium, use 160
milligrams of steel.   The steel is dissolved in 30 c.c. 1:3
sulphuric acid before the reduced chromium solution is
added to it.   Put this standardizing mixture through all
of the analytical operations given for the actual analysis
of the ferro-chromium, including the addition of the nitric
acid.

CALCULATIONS.

The ferrous am. sulphate used by the 0.500 gram $K_2Cr_2O_7$ is,
for example, 102.6 c.c.   The percentage of chromium in the
dichromate is 35.38.   Therefore $0.500 \times 35.38 \div 102.6 = 0.001724$,
or 1 c.c. of dichromate equals 0.001724 gram of chromium.

A check standardization using 0.600 gram of $K_2Cr_2O_7$ gave
1 c.c. equals 0.001713.   The average value is 0.001718.   Suppose
0.300 gram of a ferro-chromium required 99.9 c.c. of the sul-
phate standard: $99.9 \times 0.001718 \div 0.3 = 0.5721$, or 57.21 per
cent chromium.

CARBON.

The total carbon can be obtained quickly by the means
of some oxidizing flux in a stream of oxygen.   Direct
combustions with oxygen alone are very incomplete, at
least with temperatures of 950° C. and under.   Decarbonize

one gram of 60-mesh sample with four grams of red lead, either in the gas or electrically heated furnaces. See pages 132, 150, 157.

Aluminum.

Proceed as in ferro-vanadium, page 19.

Phosphorus and Sulphur.

Fuse 2 grams, twice, with sodium carbonate and niter. Fuse each time with 20 grams of carbonate and 5 of niter. Add 5 c.c. of the aluminate. Precipitate the combined filtrates from the water solutions of the fusions with 1 : 1 HCl and proceed as in ferro-vanadium, getting the sulphur by completely acidulating the filtrate from the aluminum hydroxide, evaporating once to dryness, filtering and finishing by barium chloride in acid solution. Obtain blanks on fluxes and reagents and deduct the same from the barium sulphate found. A third fusion is often necessary to remove all chromium, phosphorus, aluminum and sulphur from the ferro-chrome.

Second Method for Phosphorus and Aluminum.

Fuse 2 grams of finely ground sample twice for five minutes with sodium peroxide in a nickel crucible. Dissolve in water, in a dish, as described under chrome ore. Filter after each fusion, washing with sodium peroxide water. For phosphorus the combined filtrates are treated with 5 c.c. of the sodium aluminate solution, and phosphorus and sulphur determinations are then proceeded with as in the sodium carbonate and niter fusion method: The aluminum hydroxide is precipitated by adding 1 : 1 hydrochloric acid until the former settles out well, still

keeping the solution slightly alkaline to prevent inter-
ference of the chromium. The water solutions of the
fusion should be boiled a half-hour in porcelain or platinum
vessels to remove the hydrogen peroxide before adding
hydrochloric acid to precipitate the aluminum as hydroxide,
hydrogen peroxide being a reducing agent in acid solution.

For Aluminum.

(1) First add to the filtered, hot, water solution of the
peroxide fusions 1 : 1 hydrochloric acid, and note if any
cloudiness or white precipitate forms before acidity is
reached. If a precipitate appears, it is filtered out, washed,
and examined for aluminum, silicon, and phosphorus as
given under ferro-vanadium, page 19.

(2) To the filtrate from the aluminum add 5 c.c. of
sodium aluminate and 5 grams of sodium carbonate.
Precipitate the remainder of the phosphorus as aluminum
phosphate, and proceed as already described for phosphorus
and sulphur. Add the phosphorus obtained from the
aluminum, if any is found in the ferro, to that obtained
from the added aluminate, to get the total phos-
phorus.

(3) To avoid (2), 100 mg. of metallic aluminum can be
added to (1) to insure the presence of sufficient aluminum
to carry out all of the phosphorus. The metal is added as
chloride by dissolving it in 10 c.c. of 1 : 1 HCl. Deduct
this 100 mg. from the total aluminum found to get the
aluminum in the test.

Third Method for Phosphorus, Sulphur, and Aluminum.

(A) Fuse 1 gram of the finely ground sample with 10
grams of sodium carbonate and 2 grams of niter. Dis-
solve the fusion in water. Filter, wash with sodium car-

bonate water.   Roast the residue at a low red-heat until filter paper is gone.   Dissolve the oxides in hydrochloric acid, and transfer the solution to a 1000 c.c. boiling flask. Make a peroxidation, adding 100 mg. of metallic aluminum exactly as given under the second method for phosphorus in ferro-vanadium, page 25.

(B) The filtrate and washings from the water solution of the sodium carbonate and niter fusion are examined for phosphorus, sulphur, and aluminum exactly as given under the first method for these elements.

For phosphorus, the aluminum hydroxide precipitates obtained from the peroxidation (A) and from the filtrate from the sodium carbonate and niter fusion (B) are combined by putting the hydrochloric solutions of the aluminum hydroxide precipitates together before converting to nitrates.   Finish as in the first method.

The object of this third method is to avoid all but one of the fusions required in the first method.   Deduct blanks made on all acids, sodium peroxide and fluxes used. (Either by sodium peroxide fusions or by sodium carbonate and niter fusions considerable yellow chromate color is obtained from the water solution of third fusions of ferro-chromium!)

All alkaline solutions that have been precipitated with acid should always be tested, after the aluminum hydroxide has been removed, by further addition of acid followed by a slight excess of ammonia.   If any white precipitate forms, it is collected, washed, and added to the main portion of the hydroxide.

Silicon.

Obtain the silicon as in high silicon ferro-vanadium; i.e., fuse if necessary, acidulate with hydrochloric acid, and evaporate twice to dryness.

Manganese.

Remove the chromium by zinc oxide, and proceed as in chrome steel soluble in sulphuric acid.

If fusions are required, separate the manganese by prolonged heating of the water solutions of the double fusions with alcohol as in high manganese ferro-vanadium.

Iron.

The residue from the water solution of sodium carbonate and niter fusions is treated for iron as outlined for iron in ferro-vanadium. Or the precipitates remaining on filters after separating chromium, aluminum, and phosphorus by the peroxide method can be roasted, dissolved in conc. hydrochloric acid, evaporated to fumes with sulphuric acid, reduced with zinc and titrated with permanganate solution for iron as in ferro-vanadium.

Chromium in Chrome Ore.

Fuse 0.6 gram with 8 grams of sodium peroxide in a 45 c.c. porcelain crucible. Keep the fusion molten for five minutes. Three or four melts can be made of chrome ore in porcelain before the peroxide cuts through.

Place the crucible in a 375 c.c. casserole. Cover with a watch glass. Stand the crucible in the bottom of the casserole. Allow water to flow slowly down the under side of the watch glass and drop into the open crucible. The melt promptly boils up and dissolves in a few moments. Remove the crucible. Boil the water solution, without filtering, for one-half hour to remove all hydrogen peroxide. The excess of peroxide would reduce some of the chromic acid, if allowed to remain, just as soon as the fusion is acidulated with the sulphuric acid. Add 50 c.c. *excess* of 1 : 3 sulphuric acid.

Add 2 c.c. of the ferricyanide indicator to the cold sulphuric acid solution, and titrate it as in ferro-chrome, using the same standard. Standardize by fusing 0.340 gram of potassium dichromate in 8 grams of peroxide in a porcelain crucible, and complete the operation as in actual analysis. Multiply the number of milligrams of metallic chromium found by 152.2 and divide by 104.2 to obtain the milligrams of chromium oxide in the ore.

As the samples of ferro-chromium and chrome ore are likely to vary somewhat, especially in the case of ferro-chromium, several determinations should be made of the same sample and the results averaged.

Porcelain crucibles are not suitable for fusion of *metals* with sodium peroxide, as great heat is generated, causing the crucible to crack.   This is not the case in chrome ore.

Insoluble Ferro-Chromium.

Ferro chrome that is not attacked by acids can be conveniently assayed for chromium as given for chrome ore, but as the porcelain crucible usually cracks during the cooling a new crucible is needed for each fusion.

Weigh 0.500 gram of the finely ground ferro and fuse it with 8 grams of sodium peroxide.

CHAPTER VII.

ALUMINUM IN STEEL.

WEIGH 3 grams of chromium and tungsten steel or 6 grams of plain carbon steel into a half-liter flask filled with carbon dioxide. Pour into the flask 10 c.c. 1:1 hydrochloric acid for every gram of steel. Warm until action ceases with CO_2 passing into the flask. Cool, and add a saturated solution of sodium carbonate (use a measured amount) until the iron precipitate dissolves rather slowly. Now add a slight excess of barium carbonate free from alumina. Add the carbonate in a thick paste. Fill the flask to the neck with water. Mix the contents thoroughly by repeatedly inverting the stoppered flask. Permit CO_2 to escape, occasionally, during the mixing. Allow the contents of the flask to settle twelve hours. Mix with pulp; filter and wash with water forty times to remove the greater portion of the ferrous iron.

Dissolve the residue on the filter, consisting of a mixture of tungsten, iron, aluminum and chromium compounds, with hot 1:1 hydrochloric acid. Wash the filter free of iron test. Evaporate the filtrate and washings from the solution of the residue to 20 c.c. Cover the dish with a watch glass and add an excess of potassium chlorate. Heat with cover on until all spraying is over. Remove the cover and evaporate to dryness. Add 20 c.c. conc. hydrochloric acid. Cover and boil gently until all is in solution except a yellow residue of tungstic acid, which will appear if the steel contains tungsten. Add 50 c.c. of water. Boil twenty minutes. Filter. Wash

with 1 : 20 hydrochloric acid until the filter no longer gives an iron test. Evaporate again to dryness. Dissolve, filter and wash as before. Precipitate the filtrate and washings with a slight excess of ammonia in a casserole. Boil a few minutes. Add paper pulp; use ashless pulp. Filter. Wash with ammonium nitrate water until free from chloride test. Use the same number of filters on all tests and on the blank test. The latter is made at the same time as the regular analysis. Roast off the paper in a large platinum crucible, and fuse the ash with 10 grams of sodium carbonate and 2 grams of niter, keeping it molten for a half-hour. Leach out with water, filter, wash, add 1 : 1 hydrochloric acid to this fusion a c.c. at a time until the aluminum separates out in a white flocculent precipitate if present in considerable quantity, or until the solution looks milky if the percentage is small. Be sure to keep the solution at all times distinctly alkaline, or much vanadium and chromium, if any be present, will be carried out with the aluminum. Proceed further as in ferro-vanadium. See aluminum in ferro-vanadium, page 19.

The aluminum gives only a faint cloudiness to the solution if present in small quantity. In the latter case wait two hours before filtering.

Fuse the iron residue a second time. Dissolve melt in water. Filter; wash; precipitate with acid. If much precipitate of aluminum hydroxide, etc., is obtained from the second fusion, then fuse a third time and proceed as before. Combine all three precipitates of aluminum hydroxide and finish as given under aluminum in ferro-vanadium, page 19.

Run a blank including all chemicals and filter-paper pulp; deduct the aluminum so obtained from the final weight of Al_2O_3.

Second Method.

Proceed as in the first method until the hydroxide precipitates have been obtained with ammonia. (After the chlorate treatment; the subsequent evaporation to dryness; and removal of any tungsten that may be present.) Roast the paper from the hydroxide precipitates. Dissolve in hydrochloric acid and transfer this solution to a 1000 c.c. boiling flask, and then finish by wet sodium peroxide separation as given under the second method for aluminum in ferro-vanadium, see page 25. Deduct blanks. Remove phosphorus and silicon. Multiply the pure Al_2O_3 by 53.033 and divide by the weight taken for analysis to obtain per cent of aluminum.

The separation of aluminum from iron by sodium peroxide has some advantages. If the operator thinks he has carried the addition of the HCl too far, he can redissolve the hydroxide right in the solution by adding a slight excess of the peroxide. Then the precipitation can be repeated with more caution after the usual 20 minutes' boiling to remove the excess of H_2O_2.

While it is not essential, it is easier to precipitate aluminum hydroxide free from vanadium and chromium if some sodium carbonate is present. The carbon dioxide causes the aluminum hydroxide to precipitate while the solution in which the precipitation occurs is still alkaline. For this reason ten grams of sodium carbonate are added to all solutions from which aluminum is to be precipitated by HCl unless the carbonate is already present.

CHAPTER VIII.

COPPER IN STEEL AND PIG IRON.

DISSOLVE 15 grams of drillings in 300 c.c. of 1.20 nitric acid in an 800 c.c. beaker. Heat until all action ceases. Add an excess of $KMnO_4$ solution same strength as used for phosphorus in steels. Boil gently for 30 minutes. If the $KMnO_4$ disappears during the boiling, add more of it. Steels require 4 to 8 c.c. and pig iron 25 to 30 c.c. of the permanganate solution.

In pig iron add 5 c.c. of hydrofluoric acid before boiling with permanganate of potash. Heat ten minutes. Then boil with the $KMnO_4$ solution.

After boiling the pig iron or steel with permanganate solution, add enough wet pulp to nearly fill a 50 c.c. graduated cylinder. Filter through double 12 c.m. filters into an 800 c.c. beaker. Wash the pulp, etc., free from iron with a dilute nitric acid wash consisting of 5 c.c. of 1.20 nitric acid diluted with 200 c.c. of water. This takes about 40 washings.

To pig iron or steel containing 0.010 to 0.030 per cent of copper, add at this stage 20 c.c. of a solution of potassium ferricyanide made by dissolving 5 grams of the crystals in 120 c.c. of distilled water. Stir thoroughly and permit the solutions to stand.

If the copper content is unusually high, add two c.c. of the ferricyanide solution for every milligram of copper supposed to be present in the steel. If nickel is present, it is precipitated with the copper, but forms more slowly.

As there is a tendency to form blue cyanide of iron the filtrations should be proceeded with in about a half-hour. Add as much paper pulp as in the first filtrations, filter and wash five or ten times with water containing 5 c.c. of ferricyanide solution per 100 c.c. of distilled water. Use a 15 cm. filter.

Roast off the pulp in a porcelain crucible. Dissolve the iron and copper oxides with 5 c.c. of conc. hydrochloric acid. Rinse the solution into a 200 c.c. beaker. Dilute to 150 c.c. with water and pass H_2S for a half-hour at a rapid rate. This removes the copper from nickel and any iron that may have been precipitated as cyanide.

Filter on a small filter; wash twenty times with H_2S water. Burn the paper in a 45 c.c. porcelain crucible. Dissolve the oxide in 20 c.c. 1.20 nitric acid, warming until all black residue is dissolved except perhaps an occasional flake of carbon from the filter paper. Rinse the solution into a 5-ounce beaker, keeping the volume as low as possible for copper of 0.020 per cent and under, in order that the blue color with ammonia may be distinct. Copper as low as 0.015 per cent gives a distinct blue if properly manipulated. Now add a saturated solution of sodium carbonate, a little at a time, until a precipitate forms. Then add 0.5 c.c. of conc. ammonia. Titration follows with a standard solution of potassium cyanide made by dissolving 2.244 grams of potassium cyanide and 5 grams of stick potassium hydroxide in water and diluting to 1000 c.c. 1 c.c. of this standard should equal about 0.00064 to 0.00069 gram of metallic copper. Standardize the solution by adding 10 and 15 milligrams of metallic copper of 99.8 per cent Cu to 15 grams of any steel or pig iron. Weigh out also two 15-gram portions of this same steel or iron, but add no copper to them. Put all four weights through the entire operation, titrating each one to the disappearance of the blue as given under "Titration."

Titration.   Place a 5-ounce beaker containing distilled water beside the one containing the copper to be tested. Add the cyanide standard to the test until it is as free from even a slight blue tint as the beaker of distilled water.

This method has been tested with known amounts of copper added to steels, and with steels standardized by the old standard methods.   It is much more rapid, and results check very satisfactorily.   Filtrations might be hastened by using pulp filters on porcelain plates and applying slight suction.

CALCULATIONS.

Pig Iron Sample.

(1) 16.0 second reading of burette.
    7.9 first reading of burette.

    8.1 equals c.c. of standard used.
        No copper added.

(2)   48.0
    15 mg. copper added 16.2

                31.8 equals c.c. of standard used.

(3) 10 mg. copper added 23.6
                 0.0

                23.6 equals c.c. of standard used.

(4) $31.8 - 8.1$ equals c.c. of standard used by 15 mg. Cu.

(5) $23.6 - 8.1$ equals c.c. of standard used by 10 mg. Cu.

(6) From (4) we have $15 \div 23.7 = 0.632$, or 1 c.c. of cyanide equals 0.000632 gram Cu.   ($0.998 \times 15 \div 23.7$.)

(7) From (5) we have $10 \div 15.5 = 0.643$, or 1 c.c. of cyanide equals 0.000643 gram Cu.   ($0.998 \times 10 \div 15.5$.)

(8) From (1) we have $8.1 \times 0.00064 \div 15 \times 100 = 0.0345$, or 0.0345 per cent copper in the sample of pig iron, fifteen grams having been taken for analysis.

QUALITATIVE VALUE.

With two grams of sample, as little as 0.1 per cent of copper gives a very noticeable yellowish cloud when the potassium ferricyanide is added to a solution of steel treated as described. Hence the method affords a rapid qualitative test for the presence of copper in sufficient quantity to be injurious (0.05 per cent and over) for *most* purposes for which steel is used. The operator can easily decide whether the precipitate is copper or nickel. If it is copper, the precipitation is almost instantaneous. If it is nickel, the reaction is noticeably slower and the precipitate is of a brown color, closely resembling that of iron hydroxide. A yellowish cloud, forming, at once, on the addition of the first c.c. of the precipitant, is characteristic of copper. If this be followed by a more slowly forming brown precipitate,* then both elements are present. Many makers of tool steel insist that the copper content of best tool steel be under 0.02 per cent. Several steels doing fine work, however, have been analyzed by the author and found to contain copper greatly in excess of this limit. It is largely a question of what sort of a tool is to be made from the steel.

The tendency to form blue ferricyanides of iron on adding potassium ferricyanide to ferric solutions, the author has found, can be eliminated sufficiently to prevent serious clogging of filters, by keeping the iron solution somewhat neutral, after *first boiling it with* an *excess* of permanganate solution and filtering out the excess of manganese oxide. After removing the latter by filtration, add 1:1 ammonia until the hydroxide of iron dissolves rather slowly. Then add the ferricyanide and proceed as already described.

As the copper ferricyanide precipitates almost instantly, forming a very considerable cloud of yellowish precipi-

* Add at least 20 c.c. of the ferricyanide when testing for nickel.

tate even with 0.03 per cent copper, it is very finely divided, and has a tendency to run through the filter. The first portion that is filtered should be poured back on the paper until it runs through clear. Then proceed with the filtration. Stand the main filtrate aside when washing begins, and, should the latter be cloudy, filter with a little pulp on a small filter and add it to the main precipitate.*

When precipitating a large quantity of copper by this method,— for example, sixty or one hundred milligrams,— the nearly neutral solution should be largely diluted, making the volume about 800 to 1000 c.c. before adding the precipitant. See Separation of Copper and Nickel from Vanadium by Ferricyanide of Potassium.

* Pay no attention to any clouding of the filtrate that may occur after the latter has stood for some time.

CHAPTER VIII.

Part II.

SEPARATION OF NICKEL AND COPPER FROM IRON AND VANADIUM BY POTASSIUM FERRICYANIDE.

Proceed as outlined for copper in steel, except smaller weights of sample are usually required.

For nickel and copper in ferro-vanadium dissolve one or two grams of sample, using 30 c.c. of 1.20 nitric acid for each gram. If the ferro is high in silicon, carbon and aluminum, and for this reason only partly soluble in nitric acid, add a few c.c. of hydrofluoric acid to the solution after action with nitric acid is over. Heat until all metallic or gritty particles are in solution. Or the insoluble part can be broken up by a sodium carbonate and niter fusion; dissolved in hydrochloric acid; the latter removed by evaporation to fumes with sulphuric acid; the sulphate dissolved in water and returned to the main solution. Then boil the latter with an excess of permanganate solution; filter out the manganese oxide as described under Copper in Steel. To the filtrate and washings 1:1 ammonia is added until a slight precipitate of hydroxide is obtained that dissolves slowly. The copper and nickel are precipitated with potassium ferricyanide as in Copper in Steel. Large amounts of nickel — i.e., 0.025 to 0.050 gram — precipitate quickly, but smaller quantities should be permitted to settle for one hour before filtering. It is best to let all nickel tests stand at least one hour. Add as much paper pulp from ashless filters as will nearly fill a 15 c.m. filter. The precipitate and pulp are filtered out; washed a few times; dried; ignited in a large porce-

lain crucible; the ash transferred to a 6-ounce beaker; dis-
solved in 30 c.c. of aqua regia.   Clean the crucibles with
10 c.c. of the latter and add the cleanings to the main part.
(Nickel oxide dissolves with some difficulty, requiring con-
siderable heating).   50 c.c. 1:3 sulphuric acid are added
to the solution; evaporated to 12 c.c.; diluted to 300 c.c.;
the copper precipitated with H_2S; filtered out and washed
thoroughly with H_2S water and finished as in steels.   The
filtrate and washings from the H_2S precipitation will con-
tain all of the nickel and a little iron.   Evaporate this fil-
trate and washings to 50 c.c., and add 30 c.c. of conc. nitric
acid to oxidize the iron and destroy any remnant of the H_2S.
Heat with a cover on the dish until all action is over.   Then
remove the cover, cool, add 30 c.c. 1:3 sulphuric acid and
evaporate until slight fumes of sulphuric anhydride are
obtained.   Cool; add 50 c.c. of water and filter into a
600 c.c. beaker.   Add 10 grams of citric acid; make faintly
ammoniacal; cool and titrate the nickel with potassium
cyanide.   See the author's modified cyanide method for
Nickel in Steel, page 104.

If it is desired to determine a very small quantity of
nickel in steel, about 0.3 per cent and under, weigh
10 or 15 grams of sample and proceed as outlined,
getting the nickel and the copper from the one analysis.
If the nickel content is likely to be under 0.1 per
cent, it is convenient to use 10 grams of sample.   If it
is in excess of 0.2 per cent, it is best to use 5 grams.   The
precipitate requires that considerable paper pulp be mixed
with it to secure rapid filtrations.   Wash the pulp, etc., five
times with water containing a drop of sulphuric acid and
5 c.c. of the ferricyanide solution per 100 c.c. of water.
As the precipitate has a tendency, at times, to run through
the filter when first poured on it, this first portion of the
filtrate is refiltered until it is clear.   When filtering large
precipitates, such as would be obtained from 50 milligrams

of nickel, it is expedient to use two funnels to hasten mat-
ters.   Nickel up to 50 milligrams from a five gram weight of
sample, or 10 milligrams of nickel from 10 grams of sample,
can be conveniently precipitated from a volume of 500 c.c.
For large amounts of nickel in steel,— i.e., 0.50 per cent and
over,— the foregoing method is not nearly so rapid as the one
described on pages 104–115, but for minute quantities, or
where it is necessary to first remove the bulk of the iron or
the vanadium (Much vanadium in solution gives ammonia-
cal citrates of an almost black-green color, greatly interfer-
ing in the method just referred to.), it is an indispensable
preliminary to the cyanide titration.   There would seem to
be no reason why the ferricyanide could not be applied,
with suitable modifications, to the determination of copper
and nickel in ferro-manganese, chrome and other ferros
and metals that are not precipitated by this useful reagent
(notably aluminum) in acid solution.   Manganese is precipi-
tated by the ferricyanide in neutral or slightly ammoniacal
solution as quickly as are copper, nickel, and zinc in slightly
acid solution.   See the author's volumetric method for
all percentages of manganese above 2 per cent, page 123.

By the above process the copper and nickel can be
determined, quantitatively, in the same analysis with the
chromium and the vanadium when the copper does not
greatly exceed 0.25 per cent: Two grams are taken for
the analysis.   The nickel and copper ferricyanides are
filtered out after the regular titrations have been made
for V and Cr.   Of course no time must be lost in making
the vanadium part of the titration, as copper soon clouds
the solution after the addition of the ferricyanide.   The
author uses this scheme to get Cr, V, Ni, and Cu from the one
analysis.   In such cases the titrated solution is allowed to
stand a half hour before filtering.   If brown nickel ferri-
cyanide begins to appear, 40 or more c.c. of potassium
ferricyanide are added and filtration is delayed for an hour.

CHAPTER VIII.

COPPER IN METALLIC COPPER — VOLUMETRIC.

The author regards the following cyanide titration as a simple and rapid method for the assay of metallic copper. Scarcely any element interferes that cannot be removed by precipitation with H_2S in hydrochloric acid solution. If carried out with proper attention to details, there is no more accurate volumetric method in commercial use. It is essential that the potassium cyanide be standardized with metallic copper of known copper content, or by some recrystallized c.p. salt of copper. The metal is preferable, and is put through every analytical detail that is applied to the analysis of the test.

Operate with 0.5 gram of the test and of the standard copper drillings, running both standardizations and tests parallel with each other. Use copper of 99.8 per cent purity for standardizing. The drillings are dissolved in 10 c.c. 1.20 nitric acid, evaporated to 5 c.c., filtered from any tin, etc.; the filter washed with water containing a little nitric acid. The filtrate and washings are evaporated to fumes with 20 c.c. 1 : 3 sulphuric acid. The copper sulphate is dissolved in water. Any lead is removed by filtration and washed with water containing a little sulphuric acid. Hydrogen sulphide is then passed through the filtrate, in a volume of 400 c.c., with 5 c.c. excess of 1 : 1 hydrochloric acid for every 100 c.c. of water, until the copper has completely separated in hot solution. Filter. Wash with H_2S water. Return filter and all to the

beaker. Add 50 c.c. of 1.20 nitric acid. Give standardi-
zations and test the same excess of acid. Warm with a
cover on until copper sulphide is dissolved. Filter out
pulp. Wash thoroughly with water containing a little
1.20 nitric acid. Ignite the pulp; dissolve the residue in
1.20 nitric acid; add the solution to the filtrate and
washings; evaporate to 20 c.c. Add 1.5 grams of citric
acid and a slight excess of sodium carbonate. Use a
saturated, filtered solution of the carbonate and add it
until effervescence ceases entirely. Titrate the clear
blue solution with a standard of potassium cyanide made
by dissolving 22.434 grams of the best cyanide together
with 5 grams of potassium hydroxide in distilled water
and diluting to one liter. One c.c. of this standard
usually equals about 0.00635 gram of copper; but this
value should always be fixed by the operator himself, in
the manner just outlined. The following modification
removes uncertainty as to the end point when titrating
large amounts of copper. Add the potassium cyanide as
usual until the blue color is almost gone. Follow with
additions of a cyanide standard of one-fifth strength
until all blue tint has disappeared. Then add 2 c.c.
of a 20 per cent solution of potassium iodide in water;
then silver nitrate standard until a slight cloud of silver
iodide is formed as in Nickel in Steel. (Chapter IX.)
Now add about 10 c.c. excess of this dilute cyanide
standard. Again add the silver nitrate standard until a
slight milkiness is produced in the solution; 2.925 grams
of silver nitrate are dissolved in water and diluted to
500 c.c. for this work.

STANDARDIZATION.

Suppose 0.500 gram of copper drillings of 99.8 per cent
purity were taken, and that after putting this metal

through all of the foregoing analytical operations the following data were obtained:

First, The concentrated cyanide standard required to *nearly* discharge the blue color equals 76.9 c.c.

Second, The one-fifth cyanide standard required to *entirely* discharge the blue equals 26.8.

Third, The silver nitrate solution needed to produce a slight milkiness in the solution, after the blue color was entirely gone, equals 13.6 c.c.

Fourth, 8.3 c.c. of silver nitrate were used to produce a cloudiness, again, after the addition of 11.3 c.c. of the one-fifth cyanide standard in excess, or 1 c.c. of $AgNO_3 = 11.3 \div 8.3$, or 1.36 c.c. of the one-fifth cyanide standard.

Fifth, Therefore $26.8 - (13.6 \times 1.36) = 8.3$, or the amount of one-fifth cyanide used in reaction with the copper, or 1.66 c.c. of conc. cyanide to be added to 76.9, or a total of 78.56 c.c. of conc. KCN required to combine with the 0.500 gram of 99.8 per cent pure copper. Hence 1 c.c. of the concentrated cyanide standard equals $0.499 \div 78.56 = 0.00635$, or 1 c.c. $= 0.00635$ gram of copper.

Mr. R. M. Clarke of this laboratory suggested that it might be an advantage to use silver nitrate to obtain a more exact end point instead of relying on the disappearance of the blue. The analytical details are the author's.

Further Details.

(a)

Stir the copper sulphide into small particles before heating it with the 1.20 nitric acid, or an insoluble black lump may form. Then heat very gently at first. Keep the temperature considerably below 100° C. at all times to prevent occlusion of some of the copper sulphide by the liberated sulphur, and the formation of a black insoluble residue. Pay no attention to any milkiness

that may appear when the nitric acid solution of the pulp ash is added to the nitric solution of the main sulphide.

(b)

The titration can be accurately accomplished, omitting the one-fifth cyanide standard: Add the concentrated standard until the blue is entirely gone. Then add the KI indicator and follow with the silver nitrate until a very slight permanent cloudiness occurs. Next drop into the beaker an excess of 5 c.c. of the conc. cyanide. Again add the silver nitrate until a very faint milkiness is once more apparent that does not disappear after 15 seconds stirring.

(c)

Further, it is quite important to add the cyanide, while discharging the blue color, very slowly when the latter begins to fade: Add the standard three drops at a time; then stir vigorously for 20 seconds. If the blue is not all gone, add three drops more and stir again for a period of twenty seconds. By proceeding in this way and making the titrations in small volumes — beginning with a volume of not over 100 c.c. — the disappearance of the blue affords an accurate end point but more experience and judgment is required than when using the cyanide and "silver" scheme. After thus carefully removing the blue tint proceed to determine the actual cyanide used by means of titration (b).

Calculations.

(1) 0.500 gram of copper required 84.2 c.c. of the concentrated cyanide to just discharge the blue.

(2) 24.8 c.c of the AgNO₃ standard were required to produce the *first* faint cloudiness.

(3) 21.9 c.c. of AgNO₃ were needed to produce the second faint cloud after the addition of 5 c.c. excess of

the conc. KCN. Therefore $21.9 \div 5 = 4.38$ or 1 c.c. of the cyanide equals 4.38 c.c. of the silver nitrate standard.

(4) From (2) and (3) we have $24.8 \div 4.38 = 5.66$, or the excess of the cyanide standard in the solution. From (1) $84.2 - 5.66 = 78.54$, or the number of c.c. of the cyanide required to combine with the 0.500 gram of copper. There is always an excess of the cyanide when the blue color is gone.

TITRATION OF COPPER IN THE PRESENCE OF OTHER METALS.

If the solution contains 3 grams of citric acid and a moderate excess of the sodium carbonate, 0.500 gram of copper can be accurately titrated in the presence of 0.100 gram of zinc, or iron, or 0.050 gram of lead: The citric acid is added to the nitric solution of the metals; then the carbonate until effervescence ceases, and 5 c.c. in excess. The volume before titration should be about 100 c.c. When much iron is present the alkaline solution is a dark green. The cyanide standard is added until the green is gone and the clear amber color of the citrate of iron appears. Then determine the excess of the cyanide as usual.

As much as 0.100 gram of arsenic can be present without having the slightest effect.

The author made entirely successful titrations of 0.500 gram of copper dissolving with it 0.200 gram of antimony; also in the presence of 0.100 gram of cadmium. The end point given by the disappearance of bluish tints from the white antimony oxides and cadmium carbonate was noted. This end point was obtained as in (c). The precipitates were then removed by filtration through double filters, and the excess of cyanide was determined in the filtrate and washings in the usual

way with silver nitrate. The precipitates had to be poured through the filters several times to secure clear filtrates. The precipitates were washed ten times with dilute sodium carbonate water.

When titrating copper in the presence of 0.200 gram of bismuth the disappearance of the blue was taken as the end point, as the basic bismuth clouded the solution. With but 0.100 gram of bismuth in solution the entire titration, as outlined in (*b*), was successfully carried through before the solution was perceptibly clouded.

Large quantities of manganese interfere with the titration of copper only in so far as dark colored solutions are formed when the cyanide is added, thereby obscuring somewhat the end point between the cyanide and the "Silver." More citric acid is required. Add to the standardization about as much manganese as there is likely to be in the copper that is to be assayed. Use at least six grams of citric acid per 0.200 gram of Mn.

PRECIPITATION BY ALUMINUM.

When using this well-known method one can proceed as at first described until the filtrate and washings from the lead sulphate are obtained. Evaporate the former to 20 c.c.; add 10 c.c. 1:3 sulphuric acid and a piece of aluminum $1\frac{1}{2}$ inch square by one-sixteenth inch thick. Heat nearly to boiling for 30 minutes, or until the solution is colorless. Remove the aluminum and decant the solution through a 9 cm. filter; wash the filter 15 times with water containing a few drops of 1:3 H_2SO_4. Return the filter to the 150 c.c. beaker in which the precipitation was made.

The filtrate and washings from the metallic copper should be tested with H_2S and, if a brown coloration is obtained, continue to pass the gas until the small precipi-

tate of copper collects. Filter it out; wash it with H_2S water containing a drop or two of $1:3$ H_2SO_4. Put this filter in the same beaker with the metal; add 20 c.c. 1.20 nitric acid; heat below boiling until the copper is dissolved; filter off the pulp; wash it 40 times with water containing a little 1.20 nitric acid; evaporate the filtrate and washings to 20 c.c. in a 600 c.c. beaker and titrate the copper with cyanide and "Silver."

CHAPTER IX.

* THE RAPID DETERMINATION OF NICKEL IN THE PRESENCE OF CHROMIUM, IRON AND MANGANESE.

In applying the method of T. Moore † to the determination of nickel in steel, the directions given on page 183, Analysis of Steel Works Materials by Brearley and Ibbotson, were followed: One gram of steel was dissolved in a 150 c.c. beaker with ten c.c. of concentrated hydrochloric acid diluted with an equal volume of water.

When action ceased ten c.c. of nitric acid (1.20) were added, and the contents of the beaker were boiled to about one-half. 16 c.c. of dilute sulphuric acid were poured into the solution and also three grams of powdered citric acid. The solution was stirred until the citric acid was dissolved, transferred to a 600 c.c. beaker, and rendered faintly but distinctly ammoniacal.

The nickel was titrated with a standard solution of potassium cyanide, using a measured amount of standard silver nitrate and two c.c. of a 20 per cent solution of potassium iodide as an indicator. The deep red color of the citrate of iron greatly obscures the end point. The authors complain of this color and recommend the use of a condensing lens to cast a beam of light through the darkness. In the presence of chromium the writer found that a still more somber gloom settled down over the close of the reaction. The authors mentioned, also state that this

element retards the union of the cyanide and the nickel, causing the recurrence of the cloud of silver iodide.

After struggling with the process for some time and always carefully separating the chromium, and with it the iron, in chrome steels, an attempt was made to dispel the darkness and also to avoid these tedious separations: Less citric acid per gram of steel was taken, and the dark red shaded to blackness.

Naturally, the amount of citric acid per gram of steel was then increased, that is, six grams of citric acid per gram of steel were used, and a marked improvement was noted. Still more citric acid caused a complete lifting of the shadows.

The following modified procedure was finally adopted for nickel steels after having been thoroughly tested with plain carbon steels to which known amounts of nickel had been added: Dissolve one gram of steel drillings in a 150 c.c. beaker with 20 c.c. of hydrochloric acid (1 : 1). When action ceases add ten c.c. of nitric acid (1.20).

Reduce the volume of the solution to about 15 c.c., keeping the beaker covered during the boiling. Remove the beaker from the fire and pour into it eight c.c. of conc. sulphuric acid diluted with 24 c.c. of water. The presence of the sulphuric acid is essential to a sharp end reaction between the cyanide standard and the silver iodide in the subsequent titration.

Transfer the contents of the beaker to one of 600 c.c. capacity containing *twelve* grams of powdered citric acid. Stir until the citric acid is dissolved. Render this solution *faintly* but *distinctly* alkaline with ammonia, using one part of concentrated ammonia diluted with one part of water. A large excess of ammonia causes low results. Stand the beaker in running water until it is cold. The

volume of the solution should now be about 300 c.c. Much larger volumes than 300 c.c. should be avoided, as great dilution retards the end point, causing the cloud of silver iodide to disappear and then to reappear again in a few minutes.

The faintly ammoniacal condition can be easily controlled by adding the ammonia rather slowly and noting the changes of color that ensue: The first change is to amber, then to yellowish green, then to distinct green, then to a light shade of green, then to a yellow almost matching the yellow color of the acid solution. The reappearance of the yellow tint indicates that alkalinity is nearly attained.

A little more ammonia now causes a brownish shade, which is evidence that the ammonia is in slight excess. The moderately alkaline citrate of iron obtained in the proportion of one gram of iron to 12 grams of the citric acid yields a bright greenish-yellow solution in plain nickel steels instead of being of a dense dark red shade!

To the cold solution, two c.c. of a 20 per cent solution of potassium iodide are added. From a 50 c.c. burette a standard solution of silver nitrate is dropped into the same beaker, producing with the iodide a white turbidity. The standard potassium cyanide is added with constant stirring until the cloud of silver iodide just disappears, which it does on being converted into silver cyanide. Nickel cyanide is first formed, and then the silver cyanide is produced:

(1) $Ni(NO_3)_2 + 4 KCN = Ni(CN)_2 . 2 KCN + 2 KNO_3;$
(2) $AgNO_3 + 2 KCN = AgCN . KCN + KNO_3.$
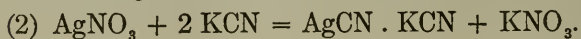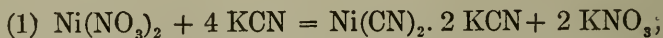
If the directions are followed as given, the titration can be accomplished at almost the full speed of the burette.

If the titrated solutions are permitted to remain in the open beakers for a time, a film usually appears on the surface of the liquid. No account is taken of it, as its presence is most likely due to a superficial loss of ammonia. The reactions are always found to be completed when the body of the solution is freed of the iodide precipitate.

Standards. From the equations as given, 5.85 grams of silver nitrate are equivalent to 4.4868 grams of potassium cyanide. This weight of cyanide dissolved in one liter of water gives a value of one c.c. equals about 0.001014 gram of nickel.

As comparatively little silver nitrate is needed with each analysis, it is not advisable to prepare more than a half-liter of the water solution of this salt, using 2.925 grams per 500 c.c. of distilled water.

The potassium cyanide standard should contain about five grams of potassium hydroxide to the liter, which renders it quite permanent. The solutions are readily standardized by applying them to a plain steel to which a known amount of nickel has been added. The chemically pure double sulphate of nickel and ammonium is a convenient standardizing medium. For example, 0.2 gram and 0.25 gram of the double sulphate can be weighed into 150 c.c. beakers together with one gram of plain carbon steel drillings.

This mixture is then put through all of the foregoing manipulations and titrated with the cyanide solution that is to be standardized. The number of c.c. of the silver nitrate and of the potassium cyanide solution used in this titration are noted. An excess of 10 c.c. of the cyanide is now added and in turn titrated with the silver nitrate solution until a distinct cloud of silver iodide is produced. This second titration gives the relation between the silver solution and the cyanide.

An actual case will illustrate the calculations: In sample

No. 3477, 1.7 c.c. of standard silver nitrate solution were required to produce a distinct turbidity and also to combine with any excess of potassium cyanide standard.   In all, 35 c.c. of the cyanide were consumed in the titration. When the cloud of silver iodide had just been dispelled, an excess of 9.8 c.c. of cyanide was allowed to flow into the clear solution.   Just 10.1 c.c. of silver nitrate standard were needed to produce a reappearance of the cloudiness. Therefore $9.8 \div 10.1 = 0.97$, or 0.97 c.c. of cyanide standard solution equals 1 c.c. of silver nitrate.   Hence instead of deducting 1.7 c.c. from 35 c.c., 1.7×0.97 or 1.65 c.c. were deducted, leaving 33.35 c.c. of cyanide combined with the nickel in this steel.

To a plain carbon steel 0.200 gram of double sulphate of nickel and ammonium were added put through all of the steps of a regular analysis.   This mixture required 28.75 c.c. of cyanide.   The nickel salt contains 14.86 per cent of nickel, or $0.200 \times 0.1486 = 0.02972$ gram of nickel were present. Hence $0.02972 \div 28.75 = 0.00103$, or 1 c.c. of standard cyanide solution is equivalent to 0.00103 gram of nickel. No. 3477 as has been stated required 33.35 c.c. of the cyanide standard, and therefore contains $0.00103 \times 33.35 = 0.03435$, or 0.03435 gram of nickel, or 3.435 per cent.

Chromium-Nickel Steels.   When chromium is present proceed exactly as in plain nickel steels except that twenty-four grams of citric acid per gram of steel are used.   This proportion of citric acid is adequate to render the end point quite as easy to see as in ordinary nickel steels.   The action is prompt and free from recurrence of turbidity. Of course, cloudiness through the entire solution will occur, as the ammonia is dissipated from it, after it has stood for some time in an open beaker.

The tabulation (1) that follows furnishes satisfactory proof that chromium does not interfere with the successful technical estimation of nickel in its presence:

TABLE 1.

Sample.	No Chromium Added. Nickel Found. Per cent.	Per cent of Chromium Added to a Portion of the Same Steels.	Nickel Found after the Addition of Varying Amounts of Chromium.
Number.			
525	5.09	4.	5.10
2991	4.44	2.	4.45
7239	3.24	1.	3.28
3017	4.96	1.	5.03
612	3.47	0.5	3.47
7273	3.29	1.	3.31
622	3.56	0.5	3.56
7288	3.32	2.	3.41
7289	3.11	2.	3.16
663	3.57	6.	3.59
2991	4.44	3.	4.47

The chromium was introduced in the form of recrystallized chemically pure potassium dichromate. The dichromate crystals were mixed with a weighed amount of nickel steel drillings before the addition of the 20 c.c. of hydrochloric acid. The combined action of the nascent hydrogen from the steel, the excess of boiling hydrochloric acid and the ferrous chloride, reduced the chromate to chromic chloride, thus duplicating the conditions found when a chromium-nickel is similarly treated.

Determinations by this modification of the cyanide method can be finished in from 45 to 50 minutes, either in the presence or absence of any per cent of chromium likely to be met with in steels or alloys soluble in the acids given. In this laboratory *duplicate* determinations in nickel or nickel-chromium steels are made in the time just specified. By the process one can decide in a few minutes whether or not nickel is present in a given steel and just how much. Tungsten, if present, does not interfere, appreciably, as has been noted by the authors mentioned in this article. The writer had two different amounts of nickel added to a steel

containing several per cent of chromium and 16–17 per cent of tungsten. This steel was then carried through exactly as though no tungsten or chromium were present, using the method as given for chromium-nickel steels.

Nickel Added, Gram.	Nickel Found.
0.0297	0.0299
0.03715	0.0372
None	0.0006

Tests were then made in the same manner in the presence of molybdenum and vanadium as follow:

TABLE 2.

Name.	Kind of Steel or Mixture.	Nickel Added. Gram.	Nickel Found. Gram.
J. R. Steel.....	Contains 10% ± Mo...........	0.0297	0.0295
Do........	....do........................	0.0222	0.0223
Do........	....do........................	None	0.0002
Bxx–173 steel .	Contains 4% Mo and 4% Cr....	0.0223	0.0222
Do........	....do........................	0.0297	0.0296
Do........	....do........................	None	0.0004
A mixture.....	0.920 gram of steel.............	0.0297	0.0298
....	0.030 gram of nickel...........	....	....
....	0.018 gram of vanadium........	....	....
A mixture.....	0.840 gram of steel.............	0.0223	0.0227
....	0.022 gram of nickel...........	....	....
....	0.035 gram of vanadium........	....	....
A blank.......	1.000 gram of steel	None	0.0008
....	0.035 gram of vanadium........	....	....

Table 2 demonstrates that neither vanadium, tungsten, chromium, nor molybdenum, when present in the amounts given, interferes appreciably in technical analysis. These amounts represent extreme cases, especially for the vana-

dium, it being equivalent in one instance to 3.5 per cent V when one gram of steel is taken.

As copper also forms cyanides, its presence would cause results to be too high, but copper is religiously avoided in good steel making. Its presence is unlikely in greater amounts than 0.06 per cent, although the writer, on one occasion, found as much as 0.25 per cent in a low carbon steel, not a *crucible* steel, however. Crucible steel rarely contains over 0.04 per cent copper. The choice brands are under 0.02 per cent in copper.

Wishing to test the extent to which nickel could be titrated in the presence of large percentages of chromium, iron being also present, the mixtures as given in Table 3 were titrated with potassium cyanide. The various salts were weighed into 150 c.c. beakers, together with the proper amounts of steel drillings. The same proportions of hydrochloric, nitric, citric, and sulphuric acids were employed as are herein given for nickel-chromium-steels, and were applied in the same manner.

A sufficient quantity of the salts of chromium and nickel, and of the steel drillings were taken to give a total of one-half gram of metals in the mixture.

Double sulphate of nickel and ammonium $((NH_4)_2 SO_4. NiSO_4.6 H_2O)$, potassium dichromate and steel drillings free from nickel were used as sources of nickel, chromium and iron, respectively.

To obtain the nickel value of the cyanide standard under conditions similar to those existing in the mixtures tested, standardizing mixtures of these salts were prepared varying from the mixtures tested as much as 1 per cent to 20 per cent in the different constituents.

For mixtures exceeding 10 per cent of nickel, a standard cyanide solution with a nickel value of 1 c.c. = 0.0031 gram of nickel was used. The standardizing mixtures were dissolved and treated exactly as the mixtures tested.

The same method of standardization was observed in the
work recorded in Table 4.

<div align="center">TABLE 3.</div>

Per cent of Metals.			Gram of Nickel.	
Ni.	Cr.	Fe.	Added.	Found.
30	40	30	0.1499	0.1494; 0.1495
60	20	20	0.2999	0.3003; 0.2989
20	40	40	0.1029	0.1022
5	90	5	0.0250	0.0248; 0.0244
4	92	4	0.0200	0.0199
1.5	95	3.5	0.00749	0.00805; 0.00822
0.5	99	0.5	0.00249	$\begin{cases} 0.00225;\ 0.00243 \\ 0.00247;\ 0.0026 \end{cases}$
0	98.9	1.0	None.	None.

Table 3 demonstrates that nickel may be estimated by
the foregoing modified cyanide process, using the propor-
tions of citric acid as given, with sufficient accuracy for
works analysis, and indeed for most practical purposes;
even when the percentage of chromium is as much as 99
per cent, and the nickel content is but one-half of one per
cent.

The titration of the mixtures given in Table 3, and con-
taining the larger amounts of chromium, requires consid-
erable practice on the part of the operator. The work
should always be carried out in duplicate. The disap-
pearance of the cloudiness in the presence of 0.100 to 0.450
gram of chromium in a volume of 350–400 c.c., is much
more exactly observed when the mixture containing the
iodide cloud is compared, from time to time, with a *similar*
mixture which is perfectly free of this milky turbidity.   The
dilution of the deep purple, or wine color, of these ammo-
niacal mixtures of citrates to more than 300 to 400 c.c.,
renders the end point but slightly more distinct, and has

the great objection of retarding the reaction between the cyanide and the nickel. The increase above twenty-four grams of citric acid, in the solution, even to the extent of adding sixty grams of citric acid, did not relieve the density of color to any perceptible extent.

When titrating with a standard, 1 c.c. of cyanide = 0.0031 gram of nickel (three times the strength used for steels) do not also increase the strength of the silver standard to equal it, but still retain the silver nitrate standard as given for steels. A silver nitrate solution sufficiently concentrated to be equivalent, volume for volume, to the cyanide standard (1 c.c. = 0.0031 gram of nickel) on being dropped into the solution containing the potassium iodide, does not produce the usual opalescence, alone, but also forms curds of iodide that do not readily combine with the cyanide standard. The end point is reached and the main body of the solution is free of cloud while curds of silver iodide still lie on the bottom of the beaker. The weaker silver nitrate standard, or 5.85 grams of silver nitrate to the liter, produces with the potassium iodide a finely divided cloud of precipitate that combines promptly with the strong cyanide standard, giving a sharp end point. Weigh, therefore, 2.925 grams of silver nitrate, diluting to 500 c.c., and 13.4604 grams of the best grade of potassium cyanide, diluting to 1000 c.c., for titrations of solutions containing from 0.100 to 0.300 gram of nickel; 1 c.c. of this silver nitrate solution should be equivalent to $\frac{1}{3}$ c.c. of the concentrated cyanide standard (1 c.c. cyanide = 0.0031 ± grams of nickel).

The titration of nickel by potassium cyanide in mixtures containing large percentages of manganese with varying amounts of chromium and iron was also tried.

As in the experiments outlined in Table 3, mixtures were prepared to contain one-half gram of metallic substances. The same nickel and chromium salts were

employed.   Potassium permanganate crystals supplied the manganese.

The crystals of double sulphate of nickel and ammonium, potassium dichromate and potassium permanganate, were weighed into a 150 c.c. beaker with the steel drillings.   To this were added 20 c.c. of dilute hydrochloric acid.   The contents of the beaker were then boiled, after the first action was completed, until the chromate and permanganate were reduced.   An addition of 10 c.c. of nitric acid (1.20) followed, and the analysis was carried out exactly as given for chromium-nickel steels, using twenty-four grams of citric acid.   The results obtained are given in Table 4.   Sulphuric acid was added as in the process for steels.

TABLE 4.

Per cent of Metals.				Gram of Nickel.	
Ni.	Mn.	Cr.	Fe.	Added.	Found.
41	20	10	30	0.2059	0.2058
20.6	40.	20	20	0.1029	0.10228
15	60	15	10	0.0750	0.0752
1.5	95.5	1	2	0.00749	0.00762
0.25	94.9	2	2.9	0.00124	0.00122
. . . .	94.9	2	4	None.	0.00006

Table 4 gives evidence of the fact that nickel can be accurately determined in the presence of large percentages of chromium and manganese, if the conditions herein given are carefully observed.   In the hands of a practiced operator no difficulty was experienced in the analysis when as much as 95 per cent of manganese was in solution with but 0.25 per cent of nickel.

Where   large   amounts   of   reduced   chromium   are encountered with nickel, the latter can be titrated to a better advantage by boiling the sulphuric acid solution of

the sample with an excess of $KMnO_4$; filtering out the manganese oxide and then proceeding with the addition of the citric acid, etc. (see E. D. Campbell and W. Arthur, J. Am. Chem. Soc., 30, 1116-20 July, 1908). There is not the slightest need for all this extra work for any amount of chromium ever found in steel, unless it is desired to determine this element in the same analysis with the nickel. In that event use 4 grams of steel and proceed as in CrV steels; (Chapter II) and, when the solution is ready for the titrations, *divide it in two equal portions*. Finish one portion for Cr and V by the method in Chapter II. Finish ONE-HALF of the other part for nickel, adding citric acid, etc. This procedure avoids the re-oxidizing and refiltering resorted to by Messrs. Campbell and Arthur; and also any necessity of making the objectionable spot tests. It affords an easy way of getting Cr, V and Ni from the one analysis.

CHAPTER X.

FERRO-MANGANESE.

Gravimetric Method.

Dissolve one gram of sample in 50 c.c. 1.20 nitric acid in a No. 4 porcelain dish. Remove the watch glass. Evaporate to dryness. Ignite to low red-heat to destroy the carbon. Replace the cover. Dissolve in 40 c.c. conc. hydrochloric acid. Heat until fumes of chlorine have disappeared. Filter into an 800 c.c. beaker. Wash the residue on the filter with 1:10 hydrochloric acid until it is free from iron test. Wash it further with water until it is free from chlorine test. Ignite the residue in a weighed crucible and finish for silicon as in steels.

Dilute the filtrate and washings to 300 c.c. Add dilute ammonia until one drop produces a precipitate that fails to dissolve with persistent stirring. Now add one drop, only, of 1:1 hydrochloric acid. Also pour into the solution 1.5 c.c. of ammonium acetate for every 100 mg. of metallic iron supposed to be present. (The ammonium acetate solution is prepared by dissolving 50 grams of the salt in 50 c.c. water. Add dilute ammonia to this solution a drop at a time until it smells very faintly of ammonia. Add water until the total volume of the acetate solution is 100 c.c.) Heat to boiling. Boil one minute. Permit the precipitate to settle a few moments. Stir in some paper pulp. Filter hot. Wash fifteen times with water containing 2 c.c. of ammonium acetate to 100 c.c. of water.

Redissolve the precipitate with 10 c.c. of hot 1 : 1 hydro-chloric acid. Wash the filter free from iron test. Dilute the filtrate and washings to 200 c.c. and precipitate it again as before. Wash the precipitate. Combine this filtrate and washings with the original filtrate and washings. Evaporate all (after adding to the combined filtrates 5 c.c. of 1 : 1 hydrochloric acid) to 200 c.c. Filter if necessary. Add 25 c.c. of ammonium acetate solution. Heat to boiling in a platinum or porcelain dish. Add to the boiling solution 75 c.c. of a saturated solution of microcosmic salt, stirring continuously. Add a slight excess of ammonia, and continue to heat the precipitate and supernatant fluid with frequent stirring until the pink manganese phosphate changes from a flocculent slimy precipitate to a pink crystalline heavy one that settles rapidly to the bottom of the vessel. When cold, filter out the manganese phosphate and wash it with cold water until no milkiness is obtained from the washings on being acidulated with a drop or two of nitric acid and tested with a drop of silver nitrate solution.

Add 10 c.c. more of the precipitant to the filtrate and washings. If a precipitate forms after several hours, collect it; wash it as in the main precipitate. Dry the two filters containing the phosphate. Remove the latter to a large watch glass. Cover it. Burn its filter in a weighed platinum crucible at a low red-heat until all black is gone. Now add the small residue, if any, obtained from the filtrate and washings tested with 10 c.c. of the phosphate of soda and ammonia. When this residue has been burned white at the lowest possible heat, add the main phosphate precipitate and ignite it very slowly to prevent loss by dusting due to liberation of ammonia. Then raise the heat to redness until all carbon is gone. Weigh the precipitate as $Mn_2P_2O_7$. Dissolve the same in 1 : 1 hydrochloric acid, and if the solution contains any insolu-

ble matter such as silicic acid, filter it out. Wash it. Ignite and weigh it. Deduct the weight from the weight of the $Mn_2P_2O_7$, multiply the remainder by 38.73 and divide by the weight taken for analysis to obtain the per cent of manganese.

Second Gravimetric Method for Manganese.

The author has tested the following separation of iron from manganese and finds it equally as good as the acetate scheme and easier of execution. It is based on the fact that manganese is not precipitated to any great extent with the iron, by ammonia, if there be a large amount of ammonium chloride in the solution.

Proceed as in the first gravimetric process until the filtrate and washings from the silicic residue are obtained. Add 100 c.c. of 1 : 1 hydrochloric acid. Dilute to 500 c.c. Neutralize with 1 : 1 ammonia, adding sufficient excess to completely precipitate the iron. Avoid much excess of ammonia and keep the solution as cool as possible during the precipitation. Stir in considerable paper pulp to hasten the filtration and washing. Filter from the iron through large filters and wash the hydroxide pulp fifteen times with water. Better separations would most likely be obtained by washing free from chloride test at this stage, but a large volume of filtrate and washings would be obtained.

Dissolve the hydroxide off the filter with 40 c.c. 1 : 1 hydrochloric acid. Wash the filter and paper pulp free of iron. Add 100 c.c. of 1 : 1 hydrochloric acid to the second filtrate and washings and again precipitate the iron hydroxide as before. Add paper pulp, and wash. Repeat the separation a third time. Add to the first, second, and third filtrates and washings 25 c.c. of the ammoniacal ammonium acetate. The latter greatly aids in produc-

ing a crystalline precipitate of the phosphate of manganese instead of a flocculent, slimy one. Precipitate the manganese as phosphate at boiling heat from the first filtrate and washings in a No. 8 porcelain dish. The manganese in the other two filtrates and washings can be safely precipitated in their respective beakers.

If the quick nickel test (see Chapter IX, page 104) shows that considerable nickel or copper is present, these elements should be removed by hydrogen sulphide before making the phosphate precipitations. This can be done as follows: Make the filtrate from the iron hydroxide slightly acid with acetic acid and pass H_2S through it until the sulphides collect and settle out well; filter; wash with H_2S water; concentrate the filtrates and washings until crystallization begins. Dilute with enough cold water to dissolve the crystals; filter again; wash with water, alone, and then proceed with the phosphate precipitation of the filtrate as in the first gravimetric method.

Volumetric Method for Manganese.

Proceed by a bisulphate fusion as given for high manganese in insoluble ferro-titanium. Fuse 0.3 gram for 80 per cent ferro; 0.5 gram for 50 per cent and 1 gram for lower percentages of manganese.

For standardizing the permanganate solution, it is better to weigh 0.3 gram of a ferro-manganese whose manganese content has been carefully determined by the gravimetric process. Put it through the entire volumetric operation, and, in this way, fix the value of the permanganate standard in milligrams of manganese, rather than by the standardization given on page 45.

Phosphorus.

The precipitate of ferric acetate contains all of the phosphorus. It can be dissolved off the filter, evaporated to

moist dryness on *water bath*.   Dissolve the residue in 50 c.c.
of conc. nitric acid.   Evaporate to about 5 c.c.   Rinse
into a 5-ounce beaker.   Boil with permanganate and finish
the phosphorus as in steels.

The phosphorus may be determined on a separate por-
tion by dissolving one gram in nitric acid.   Evaporate to
dryness.   Ignite to a dull red.   Dissolve in HCl.   Con-
vert into nitrate.   Filter and finish as in steels.

Sulphur.

Sulphur is obtained as in steels by the gravimetric
method.

Ferro-Silicon, Silicon Spiegel and Metallic Silicon.

Silicon and Manganese.   These high silicon materials
should be fused with sodium carbonate and potassium
nitrate.   Fuse 1 gram with 20 grams of sodium car-
bonate intimately mixed with 4 grams of finely ground
potassium nitrate.   Dissolve the melt in water in a
platinum dish.   Transfer the green fluid and residue to
a large casserole.   Cover with a watch glass.   Add an
excess of concentrated hydrochloric acid, keeping the
vessel covered.   Clean the crucible with a few c.c. of the
same acid.   Add the cleanings to the acidulated fusion.
Heat until all spraying ceases.   Wash off the cover, allow-
ing the fluid to flow into the casserole.   Evaporate to
dryness on a graphite or sand bath.   Add 10 c.c. conc.
hydrochloric acid.   Warm, add 100 c.c. of water and
heat for a half-hour, or until all salt is dissolved.   Filter.
Wash the silicious residue free of chloride test.   Evaporate
filtrate and washings again to dryness.   Dissolve, filter,
and wash as before.   Dry the two residues obtained from
the first and second filtrations.   Roast off the paper from

them at the lowest possible heat to prevent loss of silica. Then gradually raise the heat and blast the residues in a weighed platinum crucible until the weight of the ash is constant. Moisten the silica, which should be white, with a few drops of sulphuric acid. Fill the crucibles nearly full of hydrofluoric acid. Add the latter cautiously, at first. Evaporate and finish for silicon as in steels. It is safer to evaporate a second time with hydrofluoric and sulphuric acids, using about one-third as much hydrofluoric acid as was used in the first evaporation, to make sure that all silicon has been volatilized.

Manganese and Iron. The filtrate from the second evaporation to dryness should now be divided into two equal portions.

First Portion.

Phosphorus and Sulphur. Precipitate with a slight excess of ammonia. Wash the precipitate with water. Dissolve it off the filter with hot concentrated hydrochloric acid, using a little sulphurous acid if necessary. Convert this solution of the iron into nitrate; boil with a little permanganate and finish for phosphorus as in steels, calculating the percentage on a half-gram basis.

Sulphur. The filtrate from the ammonia precipitation is made slightly acid with hydrochloric acid. The sulphur is precipitated with barium chloride and finished as in steels. Deduct a blank obtained on all of the fluxes and acids. If it is desired to use a larger amount of sample for sulphur, it can be determined alone on a one-gram quantity without dividing into two portions.

Second Portion.

Manganese and Iron; Manganese. This portion is evaporated to fumes with sulphuric acid. The iron is precipitated with ZnO and filtered out. The filtrate is finished

for manganese as given for high manganese in insoluble ferro-titanium of high manganese content.

The Iron.   The iron and zinc oxide residues on the filter are dissolved off with hot sulphuric acid and reduced with zinc and titrated for iron in the same manner as given for iron in ferro-vanadium.   See page 30.

The Carbon.   The carbon can be obtained by combustion of one gram of the ferro-manganese, etc., with four grams of red lead; or litharge is equally good as a substitute for the red lead.

CHAPTER X.

RAPID VOLUMETRIC METHOD FOR MANGANESE IN THE PRESENCE OF IRON, CALCIUM, AND MAGNESIUM.

THE usefulness of potassium ferricyanide in the determination of copper and nickel in steel, pig iron, and ferrovanadium led the author to investigate its quantitative application to the analysis of manganese. After considerable experimentation the following method was developed for manganese in ferro-manganese, and manganese steel. It is assumed that interfering metals, like copper, nickel, and zinc, are not present in appreciable amounts: Pulverize a pound or two of 80 per cent ferromanganese, and accurately determine its manganese content by the gravimetric methods as given. Use a ferro that tests practically free from nickel by the method described under Nickel in Steel, etc. (Pages 104–115.)

Method. Weigh 0.5 and 0.6 gram of the standard ferro into 5-ounce beakers, and also the same quantities of the sample to be tested. Dissolve these portions with 50 c.c. of 1.20 nitric acid, keeping the beakers covered with watch glasses during the slow boiling. When the action is over and all of the samples are in solution, except perhaps a few brown particles of carbon (in the case of high-carbon ferros), remove the beakers from the fire. This is done before the solutions have concentrated to any extent. Cool and rinse one of the standards into a liter beaker. Add an additional 50 c.c. of 1.20 nitric acid to insure the presence of con-

siderable salt. Dilute to 500 c.c. with water. Add 1 : 1 ammonia, little by little, with constant stirring, until the iron just begins to precipitate. Continue to add the ammonia, drop by drop, until the iron separates completely and settles. The solution should now smell but VERY FAINTLY of ammonia, and have the characteristic rather sickening sweetish smell of a nearly neutral ammonia solution.

Avoid Any Large Excess of Ammonia. Mix with the hydroxide a thick cream of precipitated barium carbonate, free from copper. About 10 c.c. of this mixture of carbonate and water are sufficient. After stirring the carbonate through the iron hydroxide there should remain enough of the carbonate to form a white spot about the size of a dollar on the bottom of the beaker. The barium salt insures a constant SLIGHT excess of free ammonia, which is necessary to produce a rapidly settling precipitate on the addition of the ferricyanide standard. Add the latter slowly from a hundred c.c. burette, at the rate of 100 c.c. every four minutes, stirring the contents of the liter beaker vigorously. A stirring rod is used with its lower end covered with a small rubber cap to prevent the cracking of the beaker. For high per cent ferros use a ferricyanide solution containing 15 grams of this salt to two liters of water.

The ferricyanide, at first, produces a nearly white precipitate with the manganese, in the slightly alkaline solution. This compound quickly changes to a brown color. As the end of the reaction between the standard solution and the manganese is neared, this flocculent precipitate collects and settles to the bottom of the beaker in one or two minutes. The substance turns bright blue on being mixed with a little ferrous iron in acid, acting in this respect like potassium ferricyanide. When all but 10 or 15 c.c. of the probable amount of standard solution needed

have been dropped slowly into the beaker, *accompanied with continuous stirring*, stop adding the ferricyanide and stir vigorously for 60 seconds more. Lay the stirring rod across the mouth of the beaker with the rubber end resting on the lip of the same and projecting about an inch beyond. Place the index finger firmly over the other part of the rod and grasp the beaker with the rest of this hand. Now pour exactly 20 drops of the fluid through a 7 c.m. filter into a 152.4 by 16 mm. test tube. If the filters are thin, use them double, for, if any of the brown precipitate were to run through, it would give an intense blue with the indicator (ferrous chloride) and a false end point. When making these tests for end point, one should have, at hand, about two dozen test tubes. Do not use the same test tube for the next trial, as these tubes gradually get a coating on the inner surface that gives a faint blue color with ferrous salts. Clean the tubes that have been used for end-point tests, first with water; then with concentrated ammonia to remove the coating; then with water to remove the ammonia; next with 1:1 hydrochloric acid; and, finally, with distilled water. The tubes are then ready for further end-point tests. To the clear filtrate, in the clean test tube, add a few drops of ferrous chloride. Compare the blue color, if any is obtained, with that of a similar tint obtained as follows: In 800 c.c. of distilled water containing three drops of 1:1 ammonia, drop $\frac{1}{2}$ c.c. of the standard ferricyanide solution. Mix thoroughly with a stirring rod. Pour just 2 c.c. of this mixture into a 152.4 by 16 mm. test tube, and add to it a few drops of the ferrous chloride. This gives a blue color of a DEFINITE depth of color. If the test gives a blue color that is lighter than the standard blue, then add another c.c. of the ferricyanide to the solution being titrated, and stir it swiftly for one minute. Have a watch at hand and stir exactly 60 seconds. If a blue color is now gotten that is deeper in

shade than that in the standard tube, then stir the solution for sixty seconds more and again filter from it just twenty drops of solution. If this filtrate gives a blue with the ferrous chloride that is darker than the standard blue, the titration is considered complete, and $\frac{1}{2}$ c.c. is deducted from the total amount of ferricyanide standard required. If the filtrate from the second testing gives a lighter blue, then 1 c.c. more of the standard ferricyanide is added to the solution being tested, and, after one minute's stirring, twenty drops are again filtered and tested with ferrous chloride. The blue of the test should now be quite a bit darker than the standard blue. Again the solution, being tested, is stirred sixty seconds and twenty drops filtered and treated with a few drops of ferrous chloride, which will most likely give a blue either matching the standard blue or a little darker. If the colors match, make no deduction from the total cyanide used.

The object of the two stirrings and testings, after each addition of 1 c.c. of the standard, as the end point is near, is to make certain that the ferricyanide is not being still slowly combined with any manganese salt that may be occluded by the voluminous precipitate. This would be shown by the blue test, taken after further stirring, being fainter in color than the test taken at the preceding stirring.

As the blue tests seem to get darker on standing, the standard blue must be made fresh each time that a test is taken from the solution being assayed. That is, two c.c. of the 800 c.c. of stock are also taken and made blue with a few drops of ferrous chloride at the same time with each twenty-drop test.

Suppose the standard ferro-manganese powder contains 79.8 per cent of manganese; that 216.3 c.c. were required of the standard to precipitate all of it and give the first and second blue tests: Then, if 0.600 gram of the standard

ferro were taken, $0.600 \times 0.798 \div 215.8 = 0.002218$, or 1 c.c.
of the standard ferricyanide solution equals 0.002218 gram
of manganese under the *conditions as given*. This factor
should be fixed by the operator.

One of the weights of the sample submitted should now
be titrated exactly as described for the standard. If a
result within 10 per cent of the standard is obtained, then
that result is sufficiently accurate for all technical purposes;
i.e., correct within less than one-half of one per cent in a
possible 80 per cent. It is advisable to make the analyses
in duplicate, and also the standardizations, using 0.5 and
0.6 gram in the case of 80 per cent ferro-manganese and
correspondingly larger amounts of lower grade ferros.
Should a very much lower percentage be found, for instance
42 per cent, then this finding is most likely 1 to 2 per cent
too low. To arrive at the exact manganese, repeat the
analysis so that the standard and the test contain as closely
as possible the same amounts of iron and manganese in
solution. For the example cited, weigh for standardizing
purposes 0.550 gram of the standard ferro, and in the same
beaker also 450 milligrams of an iron, or iron wire contain-
ing 0.05 per cent, or less, of manganese. Of the sample
to be determined, weigh 1 gram. This gives a standard
mixture and a test containing very nearly the same amounts
of iron and manganese in solution. Proceed with the
second analysis as outlined in the trial, obtaining a *higher*
factor for the standard solution (1 c.c. = about 0.002318
gram Mn).

As the chemist usually knows, within a few per cent,
beforehand, the percentage of manganese in the test,
these trial analyses are, as a rule, not necessary. He
needs only to observe the precaution of taking weights
of the standard and of the tests so as to have, in each,
approximately the same amounts of iron and manganese.
For further illustration, suppose it is desired to assay a

steel of about 13 per cent manganese. Allowing for about 1 per cent of other elements besides iron, one gram of such a steel would contain close to 130 milligrams of manganese and 860 mg. of iron. To fix the manganese factor value of the ferricyanide for the titration of one gram of this steel, weigh 0.130 ÷ 0.8, or 0.1625 gram of the 80 per cent standard ferro-manganese and 0.84 gram of a low manganese iron into the same beaker. Titrate such steels exactly as the ferro-manganese except that a ferricyanide standard of one-half the strength of that given for ferro-manganese, or 3.75 grams to the liter, is advisable. And so on for steels ranging lower in manganese content, preparing standardizing mixtures from a standard steel containing 12 to 15 per cent of manganese.

Ferricyanide standard solutions should be kept in the dark and standardized each day that they are in use. Clean the beaker and rod, after each titration, with 1 : 1 hydrochloric acid, rinsing out the acid with water before making the next titration.

Instead of standardizing with ferro-manganese, one can use c.p. permanganate of potash and iron wire, making mixtures to almost exactly imitate the probable manganese and iron content of the test. For example, suppose it is desired to analyze, at the same time, a ferro about 90 per cent Mn, one about 43 per cent and one about 80 per cent Mn. For standard take 1.3 grams of c.p. crystals of potassium permanganate, and weigh also into the same beaker 0.500 gram of low manganese muck iron and 2.5 grams of oxalic acid. Cover the beaker and add a few drops of water. After the first violent action between the permanganate and oxalic is over, add, slowly at first, 50 c.c. 1.20 nitric acid. Heat the beaker, and if the solution does not become perfectly clear, continue to add a few more crystals of oxalic acid. Heat until all brown flakes are dissolved. Then boil ten minutes; cool, and proceed

as when standardizing with standard ferro-manganese. As explained, weigh of the probable 90 per cent sample and of the probable 42 per cent sample enough to give about the same amount of iron and manganese as in the standard mixture. Of the 90 per cent sample, weigh, therefore, 0.500 gram together with 0.45 gram of the muck iron. (Electrolytic * iron has but a trace of manganese in it, and should answer well as a source of iron.) Of the 42 per cent sample weigh one gram, but add no extra iron.

If the 1.3 grams of potassium permanganate require 193.8 c.c. of the ferricyanide to combine with it and give the blue end as described, then 1 c.c. of the ferricyanide, in the presence of approximately 0.500 gram of iron, has a manganese value of $1.3 \times 0.994 \times 0.34777 \div 193.8$, or 0.002318 gram. As the so-called c.p. permanganate of potash is often 0.5 to 0.6 per cent short of 100 per cent purity, hence the introduction of the factor 0.994.

The determination of any amount of manganese in the presence of Fe, Ca, or Mg can be accomplished, in duplicate, in three hours' time by this process.

The purity of the permanganate can be checked against recrystallized c.p. oxalic acid as follows: Dissolve 1 gram of the permanganate in 150 c.c. of distilled water, acidulated with 100 c.c. of 1:3 sulphuric acid. Warm the solution *slightly*, and add to it 2.0167 grams of the oxalic acid, dissolved in 150 c.c. of distilled water. Warm the solutions a little, if necessary, until the mixture of oxalic and permanganate has become colorless. Titrate the colorless solution with a dilute permanganate standard of known oxalic value. The one used in the analysis of crucibles and plumbago answers very well. 1 c.c. of this standard equals 0.00144 gram of oxalic acid (see Analysis

* Electrolytic iron of the following analysis can now be had: Phosphorus, 0.003 per cent; Sulphur, trace; Manganese, 0.02 per cent; Silicon, 0.003 per cent; Carbon, none.

of Graphite, XIII, page 187). Suppose 25.5 c.c. of this standard are required to render the decolorized mixture a slight pink that will remain permanent for thirty seconds, therefore 25.5×0.00144 or 0.0367 equals the excess of oxalic acid in the mixture. Hence $2.0167 - 0.0367 = 1.98$, or the amount of oxalic acid oxidized by the 1 gram of the permanganate. By the equation

$$2 \, KMnO_4 \ + 5 \, H_2C_2O_4 + 3 \, H_2SO_4$$
$$= K_2SO_4 + 2 \, MnSO_4 \ + 8 \, H_2 O \ + 10 \, CO_2$$
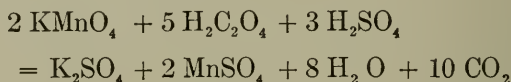
we have 316.3 grams of $KMnO_4 = 630$ grams of $H_2C_2O_4$ + $2 \, H_2O$, or oxalic multiplied by 0.502 equals permanganate; $1.98 \times 0.502 = 0.99396$, or the 1 gram of permanganate contains 0.9939 gram of 100 per cent $KMnO_4$. The precaution must be taken to use sulphuric acid that does not bleach permanganate on warming a few drops of the dilute permanganate standard with 150 c.c. of the acid.

In using potassium ferricyanide, it must be remembered that the action of the light produces a blue precipitate in it, and ferrocyanide forms which would give a blue with any little ferric iron that might be present in the indicator. At the close of the titration the solution must still smell faintly of ammonia, and an excess of barium carbonate should be visible in the bottom of the beaker. As long as the clear supernatant fluid clouds with ten or fifteen drops of the standard solution, after a wait of a half-minute, the end point is still some 10 c.c. distant. As much as 0.500 gram of pure white marble together with 0.100 gram of metallic magnesium have been added, as nitrates, to the solutions of nitrate of iron and manganese without any apparent effect on the titration of the manganese in the solution.

The reaction that takes place between the manganese and the potassium ferricyanide, in the slightly ammonia-

cal solution, is probably analogous to the one between ferrous iron and the ferricyanide:

$$2 \, K_3Fe\,(CN)_6 + 3 \, Mn\,(NO_3)_2$$
$$= Mn_3\,[Fe\,(CN)_6]_2 + 6 \, KNO_3.$$
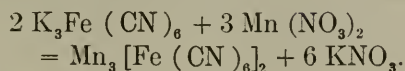
FERROUS CHLORIDE SOLUTION.

This solution for making end-point tests can be conveniently prepared from a low carbon steel with a copper content under 0.05 per cent. (If the steel contains too much copper, it will cloud with the ferricyanide.) Iron wire can be used. Dissolve 1.5 grams of the wire or steel in 20 c.c. of 1:1 hydrochloric acid, warming gently. When the solution is complete, add a few grains of granulated aluminum to entirely decolorize the iron. Then rinse the latter into a 500 c.c. stoppered flask and dilute to 250 c.c. with water. Add 5 c.c. more of 1:1 HCl and a little more aluminum. This metal keeps up a slight action with acid and prevents oxidation of the iron. It is well to make the ferrous indicator fresh each day that it is needed. Decant the 2 c.c. portions of the indicator through a small filter to remove the excess of aluminum just before using.

The author proposes to work out similar quantitative volumetric methods for the assay of copper and zinc, as both elements combine speedily with the potassium ferricyanide in slightly acid solutions.

COMPARATIVE RESULTS BY VOLHARD, GRAVIMETRIC AND FERRI-CYANIDE METHODS.

	Gravimetric.	Ferricyanide.	Volhard.
Carbonless Manganese......	{ 91.51 { 91.66	{ 91.58 { 91.47	....
High Carbon Ferro..........	{ 43.96 { 44.07	{ 43.74 { 43.68	{ 44.30 { 44.05
Manganese Steel............	13.00	12.90	....

CHAPTER XI.

THE DETERMINATION OF CARBON IN IRON AND STEEL BY DIRECT IGNITION WITH RED LEAD OR LITHARGE. *

THE writer's experience with this method for the determination of carbon, together with some notes on what led to its adoption for routine combustion analysis, may prove of interest.

The solution of steel drillings containing large percentages of chromium, tungsten or molybdenum in double chloride of copper and potassium causes more or less loss of carbon as hydrocarbon. Especially sensitive to such loss are the carbides that are separated by the double chloride from steels in which are 10 or 12 per cent of molybdenum together with several per cent of chromium.

These carbides may lose some of the carbon by contact with dilute acid, or with the oxygen of the air during washing with *suction,* or during the subsequent drying of the carbide at the temperature of boiling water.

In the spring of 1900, the writer made an analysis for carbon of a steel containing 3.8 per cent of chromium, applying the ordinary method of dissolving the borings in acid double chloride of copper and potassium, filtering on an asbestos plug, washing the carbide residue alternately with distilled water, and a mixture of one part of hydrochloric acid and twenty parts of water. The residue was then washed with water, alone, to remove the acid. After

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* A preliminary paper was read at the December, 1905, meeting of the Pittsburg Section of the American Chemical Society.

drying the washed carbide in a water-oven, it was burned with purified oxygen in a red-hot porcelain tube containing about 13 cm. of copper oxide. The products of the combustion were passed through granulated zinc of 20-mesh fineness, then through anhydrous calcium chloride, and then through phosphoric anhydride. The purified carbon dioxide was absorbed and weighed in potash bulbs. Duplicate analyses by this method failed to check.

A series of analyses of these borings were made. The acid wash *when used* was alternated with distilled water, and the washing was then completed with distilled water, alone, to remove acid.

	Kind of Wash.	Number Washings.	Carbon Found. Per cent.
1.....	20 parts H_2O to 1 part HCl	20	1.65
2.....	100 parts H_2O to 1 part HCl	20	1.52
3.....	100 parts H_2O to 1 part HCl	2	1.909
4.....	100 parts H_2O to 1 part HCl	2	1.943

In August, 1902, the process used in the foregoing, (3) and (4), was applied to a steel containing 4 per cent of chromium and 4 per cent of molybdenum with the following absence of agreement:

First analysis gave 1.28 per cent carbon.
Second analysis gave 1.53 per cent carbon.
Third analysis gave 1.33 per cent carbon.
Fourth analysis gave 1.29 per cent carbon.

The thought occurred that perhaps the carbide obtained from molybdenum steel gives up part of its carbon as hydrocarbon on being brought into contact with the air during stirring. No heat was applied to hasten the solution at any time. A number of trial analyses were made in which the time of stirring was varied and also

the acidity of the copper and potassium chloride solution. In the following, 2 grams of the drillings were dissolved in 180 c.c. of the double chloride solutions. By *acid* solution is meant a solution prepared by dissolving 600 grams of double chloride of copper and potassium in 1500 c.c. of distilled water acidulated with 175 c.c. of concentrated hydrochloric acid. By *nearly neutral* solution is meant the same as the acid solution except that but 25 c.c. of concentrated hydrochloric acid were added to the 1500 c.c. of distilled water.

The *neutral* solution consisted of 600 grams of the double chloride, 1500 c.c. of distilled water, and *no* acid. The results obtained are given in the following table:

STEEL CONTAINING 4 PER CENT MOLYBDENUM AND 4 PER CENT CHROMIUM.

Kind of Steels.	Kind of Solvent.	Time of Stirring. Minutes.	Time in the Solvent with No Stirring. Hours.	Percentage of Carbon Found.
No. 1 steel...	acid	20	....	1.53
No. 1 steel...	"	20	....	1.48
No. 1 steel...	"	10	....	1.64
No. 1 steel...	"	....	12	1.49
No. 1 steel...	"	....	24	1.52
No. 1 steel...	nearly neutral	8	....	1.60
No. 1 steel...	" "	8	....	1.55
No. 1 steel...	acid	3	....	1.60
No. 1 steel...	neutral	6	....	1.593
No. 1 steel...	"	6	....	1.606
No. 2 steel...	"	4	....	1.679
No. 2 steel...	"	6	....	1.734
No. 2 steel...	acid	4	....	1.758
No. 2 steel...	"	4	....	1.66

A combustion of the 4 per cent chromium, 4 per cent molybdenum steel (No. 2), by the red lead process described below yielded 1.734 per cent carbon.

An examination of the foregoing table shows that both

in the No. 2 and the No. 1 steels the highest result was obtained when the acid solvent was used, and also the lowest results.

Short stirring gave better agreements than the longer periods of stirring, but had evidently not eliminated all of the causes of loss. Perhaps there is loss of carbon when the carbide is being dried in the water-oven. Further, it is practically impossible to regulate the suction so as to expose the residues, during washing, to exactly the same amount of air in each analysis.

Two grams of the No. 2 steel were stirred twenty minutes with 180 c.c. of the acid solution, then transferred to the asbestos plug. Air was next drawn through the residue for fifty minutes; the amount of carbon obtained was 1.347 per cent. Two determinations of the same steel were made with sixty minutes' stirring but with the least possible exposure to air by suction; 1.63 per cent and 1.68 per cent carbon were found. In view of these results the practice was adopted of always keeping a layer of distilled water over the carbide during the washing. As soon as one layer, or covering of water, was drawn off, another was immediately supplied.

This treatment was applied to a group of ingots containing 11 per cent of molybdenum and some chromium. The neutral solution gave the higher results, as shown by the following table:

Acid Solvent. Per cent Carbon.	Neutral Carbon. Per cent Carbon.
0.52	0.60
0.46	0.56
0.53	0.59

The same process of short stirring and least possible exposure of the carbide residue to air by suction, together

with the use of a neutral solvent, was adopted for a series of ingots containing 12 per cent of molybdenum and several per cent of chromium. It failed almost completely. For convenient comparison the results obtained in these latter experiments are shown in a column parallel to those obtained, at a later date, from the same samples by the red-lead combustion method.

One well-known laboratory obtained 0.72 per cent carbon, and another, equally experienced, reported 0.64 per cent carbon on the S. H. S. sample.

Sample. 12 per cent Mo. Steel containing Cr.	Results obtained by the Neutral Solution. Per cent Carbon.	Results by the Red Lead Process. Per cent Carbon.
No. 1.............	$\begin{cases} 0.54 \\ 0.72 \end{cases}$	0.80 0.79
No. 2.............	$\begin{cases} 0.81 \\ 0.51 \end{cases}$	0.76
No. 3.............	$\begin{cases} 0.66 \\ 0.49 \\ 0.51 \end{cases}$	0.82
No. 4.............	$\begin{cases} 0.54 \\ 0.58 \end{cases}$	0.81
" 2d trial "........	$\begin{cases} 0.47 \\ 0.61 \end{cases}$	$\begin{cases} 0.88 \\ 0.85 \end{cases}$
No. 5.............	$\begin{cases} 0.61 \\ 0.88 \end{cases}$	$\begin{cases} 0.88 \\ 0.87 \end{cases}$
No. 6.............	0.49	0.73
S. H. S............	$\begin{cases} 0.69.88 \\ 0.66 \\ 0.68.75 \end{cases}$	
No. 7	$\begin{cases} 0.66 \\ 0.52 \end{cases}$	0.94 0.939
No. 10.............	$\begin{cases} 0.76 \\ 0.75 \\ 0.62 \end{cases}$	1.00
No. 11.............	$\begin{cases} 0.72 \\ 0.52 \end{cases}$	0.80

This untrustworthiness of the double chloride process for separating carbon in steel of high molybdenum and chromium content led to a search for some method of

obtaining the percentage of carbon by burning the entire substance. Having about this time noted Brearley and Ibbotson's statement that steel drillings that will pass a 20-mesh sieve and have been mixed with about three times their weight of red lead can be decarbonized in a red-hot porcelain tube, it was decided to attack the molybdenum steel in this manner. The results obtained from the molybdenum steels have been already given and need no comment.

The method was first applied to plain carbon steels, pig iron, and white iron, and was found to be perfectly accurate.

After more than eighteen months' daily use of the red lead for the determination of carbon in steel, pig iron, alloy steels, and ferro alloys, the details that have been found useful and reliable are as follows:

If part of the borings are coarse, the thin curly portions or 30–60 mesh sievings are selected. Two grams of such drillings and 2 grams of the red lead are weighed into a glass-stoppered 60 c.c. weighing-bottle. The bottle is then shaken to mix the drillings and lead oxide.

The steel sample submitted for analysis is drilled with a flat or diamond pointed drill. This style of drill will grind many of the drillings to 20-mesh fineness in the case of soft or annealed steels. If the steel be unannealed and of a carbon content ranging from about 0.35 per cent carbon and higher, thin curly drillings are obtained which decarbonize readily by reason· of thinness. If the drillings do not exceed 20-mesh, as in siftings, four grams of red lead will completely decarbonize four grams of the steel. Care is taken at all times to cover bulky drillings with the oxide of lead, as any drillings that project above the main body of the charge are likely to escape oxidation.

For soft steels and annealed steels two sieves are used. One has a 20-mesh gauze and the other one a 60-mesh gauze. Those drillings that pass the 20-mesh gauze but do not pass the 60-mesh sieve are used for analysis.

This arrangement rejects the fine dust and the thick drillings. When very small pieces of steel are received they are drilled with three-sixteenth inch diameter twist or straight drills. All sizes of the flat, or diamond point drills are kept at hand from one-quarter inch diameter to seven-eighths inch. Any good mill blacksmith can make the flat drills. By these means it is rarely, if ever, necessary to resort to the copper and potassium chloride separation of the carbon. In the laboratory of the Park Steel Co., where many combustions are made each day, covering a range from 0.04 to 3.5 per cent carbon, the writer does not recall more than a single instance in a year's time when it was necessary to resort to the double chloride process.

The mixture of lead oxide and drillings is transferred from the weighing-bottle to porcelain boats.* The Royal Meissen brand 15×75 mm. or 112×12 mm. is mostly used, being convenient sizes. The porcelain boats are slipped into † porcelain tubes of 16 mm. inside diameter $\times 600$ mm. long. Two furnaces with their porcelain tubes are operated at the same time. Until recently, the outlet ends of these tubes were filled for a distance of 125 mm. with granulated copper oxide. Later the copper oxide was found to be unnecessary. Oxygen is used during the combustion. It passes through a jar containing pieces of caustic potash (Fig. 3). It next bubbles through a solution of potassium hydroxide contained in a safety apparatus (Fig. 1), and is then dried in jars of soda-lime and calcium chloride of the design given in Fig. 3. This drying and purifying apparatus can be readily arranged and securely fastened in a space 250×406 mm.

* The author now uses the clay boats for all combustions.
† Three-fourths inch inside diameter fused silica tubes are very desirable for this work. The litharge fumes and spills, however, will, in time, destroy them. The writer sometimes uses a small inner cylinder of platinum just large enough to hold the boat. Iron oxide will flux silica tubes.

The combustions are operated in the usual manner. The portion of the tube containing the copper oxide is heated to redness, and then the remainder of the tube lying within the furnace is brought to the same temperature. The combustion tubes are constantly kept hot through half the length so that the combustion commences almost as soon as the stoppers are inserted. While the boats are being charged the oxygen is passing slowly through the
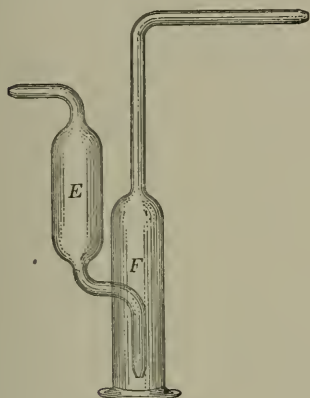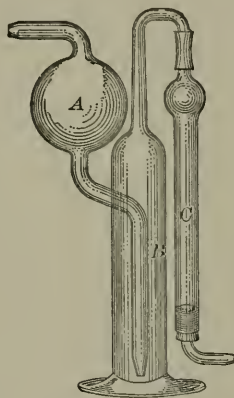
FIG. 1.   FIG. 2.

tubes and the weighing and absorbing apparatus which has been previously weighed and attached. (This weighing apparatus is shown in Fig. 2. It was designed by the writer as a substitute for the different forms of potash bulbs now in the market. It is made of heavy glass. It is easily kept clean, is not top-heavy, and does not occupy much space in a balance case.) As soon as the steel begins to burn, there is, at first, a rapid evolution of gas which quickly ceases. More oxygen is then turned into the apparatus from the steel cylinder so that a slow bubbling is maintained through the weighing apparatus. When the oxidation of the charge is completed, the oxygen begins

to rush through the apparatus at a high rate of speed. The flow of the gas is quickly checked to a normal rate, that is, it is checked so that it passes through the safety apparatus (Fig. 1) at a rate of about twenty-six bubbles per ten seconds. The stream is evenly distributed to the two combustion tubes by means of a Y-tube and screw pinch-cocks. The stream passes through the weighing apparatus (Fig. 2) at the rate of 250 c.c. every ten minutes, which is the normal speed. When the combustions are
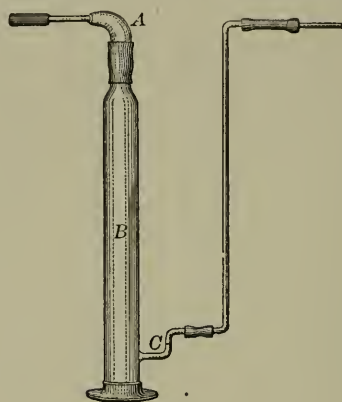
Fig. 3.

completed in both sets of apparatus, as indicated by the passage of the gas at a high rate of speed, the normal is then maintained through the red-hot tubes ten minutes longer to insure complete oxidation and that all of the carbon dioxide has been carried to the weighing apparatus. The products of the combustion pass through a purifying train shown in Fig. 4. The train connects with the glass tube leading from the outlet end of the porcelain combustion tube, by means of heavy combustion rubber tubing, at H. The gases pass through the cylinder (I) which contains a column of granulated zinc of 20-mesh

fineness. The use of granulated zinc to remove acid and chlorine in carbon combustions was first suggested by Dr. Edward S. Johnson. Cylinder I is 254×13 mm. The zinc is held in place with plugs of glass wool. The gases next enter a cylinder (J) which contains a column of phosphoric anhydride. The phosphoric anhydride powder is held in place with plugs of ignited asbestos. Cylinder J is
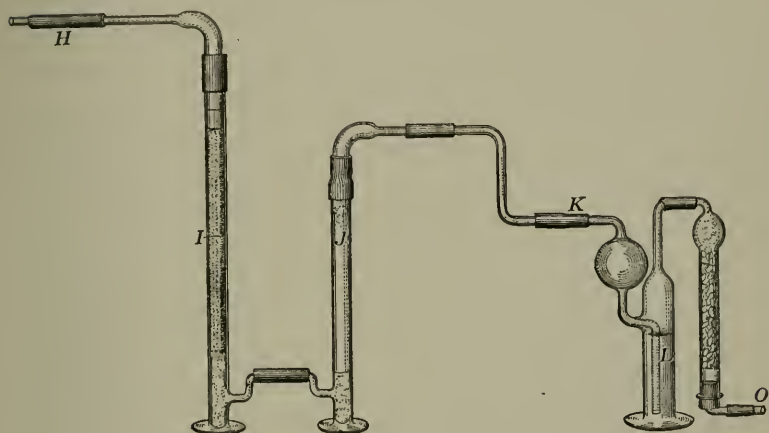
FIG. 4.

178×13 mm. Glass wool plugs should not be used in J, as they become clogged after a few combustions. Ignited asbestos is free from this objection.

The carbon dioxide, which is now freed from litharge and sulphur, and any acid fumes by zinc, and from any moisture by the phosphoric anhydride, enters the weighing apparatus (L). This weighing apparatus, as shown in the complete train (Fig. 4), differs slightly from the writer's first design shown in Fig. 2. The apparatus is charged with 20 c.c. of potassium hydroxide consisting of one part of caustic potash dissolved in one part of water. The drying tube (C), Fig. 2, is filled with small pieces of *dry* caustic

potash obtained by quickly cracking dry sticks of caustic potash in a porcelain mortar. Each end of the drying tube (C) contains a plug of asbestos or glass wool. Before inserting the rubber stopper in C, care must be taken to free the surface of the tube (C) from any moist caustic potash, as potassium hydroxide causes decomposition of rubber, resulting in continuous loss of weight.

The weighing apparatus is ready for recharging at the end of the fortieth combustion. The tare is then used for the absorbing and weighing of the carbon dioxide obtained from the next forty combustions, the exhausted apparatus now constituting the tare.

During the passage of the oxygen the outlet (O), Fig. 4, is protected from the ingress of moisture or impure air by a guard tube filled with small pieces of caustic potash. This guard tube is not shown in Fig. 4. All parts of the apparatus shown in Fig. 4 are connected by heavy-wall pure rubber tubing.

When the combustions are completed the weighing apparatus is detached from its train, and the outlet of the train is closed with a glass plug.

It is accurate to weigh the absorption apparatus (Fig. 2) filled with oxygen and thus avoid aspirations. In this way combustions can be carried through in twenty-five minutes.

The apparatus and its tare are next carefully wiped with a clean linen handkerchief and are placed in the balance case for weighing. The inlet and outlet of the weighing apparatus are kept closed with rubber caps except during weighings or when attached in the train (Fig. 4).

The method of using an exact duplicate of the weighing apparatus for a tare exposes the same amount of surface to the air during weighings and avoids the use of the larger weights.

As previously stated the porcelain tubes are kept red hot throughout one-half their length night and day so that

the combustion commences in a minute or two after the boat is inserted and the combustion tube is stoppered. The remaining burners are lighted immediately after the tube is closed.

* The red lead used in this work must be thoroughly mixed and ground free of lumps before its carbon content is determined. The so-called pure red lead costing about 9 cents per pound in fifty-pound lots is found satisfactory for the purpose. Blank combustions with 4 grams of red lead are at present yielding 6 mg. of carbon dioxide which are deducted from each determination. Blank combustions or analyses of standard steels should be made each day. The red lead is kept in tightly stoppered bottles.

The method of weighing the carbon dioxide obtained in the red lead combustions as barium carbonate was tried for several months. As it is not necessary to dry the carbon dioxide in this modification of the red lead method, the carbon dioxide was passed through a cylinder illustrated by Fig. 3 filled with granulated zinc to remove litharge fumes, and from thence the carbon dioxide entered the absorbing apparatus, which consisted of two 254×25.4 mm. test-tubes connected in tandem and containing barium hydroxide solution. The solution in the first tube converts the bulk of the carbon dioxide formed into barium carbonate, but in the higher carbon steels a little escapes into the second tube.

The barium carbonate is filtered through 12-cm. filters reinforced at the apex by a piece of cheese-cloth. The precipitate is washed thirty times with distilled water, allowing each washing to be drawn off by slight suction.

The cheese-cloth is removed and the precipitate is ignited and weighed. From this weight the amount of barium

* On one occasion a lot of red lead was purchased that was not uniform. No amount of mixing improved it. It was rejected. Subsequent kegs gave no trouble. Good commercial red lead gives about 0.004 gram of CO_2 per four grams, and is very uniform.

carbonate formed from the impurities in the red lead and that obtained from the unavoidable exposure of the excess of the hydroxide during filtration and washing is deducted. From the net weight of barium carbonate the percentage is calculated.

The barium hydroxide solutions are prepared by dissolving, or nearly dissolving, 200 grams of barium hydroxide crystals in four liters of water. It is filtered by suction through a paper pulp filter and preserved with the usual precautions. The test-tubes for the solution are provided with 30 c.c. and 70 c.c. marks. The pair of tubes constituting the absorption pair are filled to the 30 c.c. marks with water, and the barium hydroxide solution is then poured in until the 70 c.c. marks are reached.

A protracted comparison of the two gravimetric processes described in this paper extending over a period of several months was made. The method whereby the resultant carbon dioxide was weighed as barium carbonate checked excellently with the one in which the carbon dioxide was absorbed and weighed in the apparatus shown in either Fig. 2 or in the termination of the train, Fig. 4, agreeing within 0.01 per cent or less. The latter (KOH) process is preferred as requiring less manipulation, less oxygen, and less time. In the barium carbonate method it was necessary to force the oxygen through the safety apparatus (Fig. 1) at the rate of thirty-eight bubbles per ten seconds on account of the resistance to the passage of the gas through the absorption test-tubes.

The ordinary ten-burner Bunsen combustion furnace is employed, but with certain alterations to secure higher heating power. At the points where the porcelain tubes rest in the ends of the furnace these ends are slotted down about 25 mm. This permits the tubes to lie well enveloped with the flames. Further, under each foot of the furnaces pieces of fire-brick about 28 mm. thick are placed. Also

the rows of burners are lowered until they rest on the laboratory table. To keep the rows vertical one burner at each end of the rows is wired to the furnace. This lowering of the burners and raising of the furnace frame, by use of the fire-brick, improves the draught and secures hot flames with a minimum gas pressure. Strips of wet cheese-cloth about 25 mm. wide are wrapped around the ends of the porcelain tubes to keep the rubber stoppers from burning. The ends of these strips dip into suitable vessels of water.

Porcelain tubes glazed inside only, of 16 mm. inside diameter by 600 mm. long, will last from six weeks to two months when in use night and day. Flames are always kept under the tubes. Such tubes cost about $3.00 each.

Porcelain boats are cleaned for further use by allowing them to stand in nitric acid of 1.20 sp. gr. for some hours. The boats are ignited a few minutes in the flame of a Bunsen burner just before being used. Porcelain boats 14–15 mm. wide by 70–75 mm. long, Royal Meissen brand, are quoted in ten-gross lots at $14.50 per gross. These boats can be used three times.

The apparatus shown in Fig. 1 was designed as a safety apparatus to prevent the potassium hydroxide solution from blowing over into the rubber tubing from any cause. The oxygen enters the chamber E and bubbles through chamber F, which is filled to one-third its capacity with potassium hydroxide solution consisting of one part of caustic potash dissolved in one part of water. F is 35 mm. outside diameter by 170 mm. long. Fig. 3 shows a tower or jar that is used as a container for small pieces of stick caustic potash for purifying the oxygen. The pieces of apparatus shown in Figs. 1, 3 and 4 were designed by the writer to avoid the use of rubber stoppers.

* The following results attest the accuracy of the red lead process:

Name of Sample.	Weight of Sample Taken. Grams.	Weight of Lead Oxide Used. Grams.	Per cent Carbon by Red Lead.	Per cent Carbon by Double Chloride.
S. S. Co. carbon steel.......	3	9	0.395	0.415
No. 690.....................	....	....	0.985	0.96
No. 350, tungsten steel......	....	....	1.285	1.29
No. 353, tungsten steel......	....	....	1.338	1.354
No. 22, high per cent nickel steel.....................	....	....	0.698	0.696
No. 14, nickel steel	....	....	0.447	0.450
S. XIX, high per cent tungsten steel...............	....	....	{ 2.40 { 2.39	2.35
Wash metal................	1½	1½	{ 3.56 { 3.65	3.59
Wash metal................	1½	3	3.58	....
C. B. pig metal............	1½	¾	4.01	....
C. B. pig metal............	1½	1½	4.04	4.04
Soft O. H. steel No. 1.......	6	3	0.192	0.185
Soft O. H. steel No. 2.......	8	4	0.097	0.077
Soft O. H. steel No. 3761....	6	3	0.156	0.145

In July, 1901, a sample of steel was sent by Sanderson Bros. Steel Works to several laboratories. The writer retained a portion of these drillings for several years. The different laboratories reported as follows:

<div align="right">Per cent Carbon.</div>

Atha Steel Works obtained 1.25
Crescent Steel Works obtained 1.20
Park Steel Works obtained 1.214
Spaulding Jennings Steel Works obtained 1.199
Sanderson Bros.' Works obtained 1.214
La Belle Steel Co.'s Works obtained 1.20
3 grams of this sample plus 1.5 grams of red lead
     burned in stream of oxygen gave..............   1.22

In March, 1901, the following parties reported the carbon of another sample of steel:

	Per cent Carbon.
Booth, Garret & Blair reported	1.277
Sanderson Bros. reported	1.292
Park Steel Co. reported	1.301
Bethlehem Steel Co. reported	1.307
Crescent Steel Co. reported	1.315
3 grams of this sample decarbonized with 1.5 grams of red lead yielded	1.305

The writer has since had occasion to compare results with other laboratories covering a range in carbon from 0.32 to 1.45 per cent carbon with equally good agreements.

CARBON IN FERRO-CHROMIUM.

In applying the red lead process to ferro-chromium, it was found that the maximum carbon in the 65 per cent chromium alloy was obtained by burning the alloy with three to four times its weight of red lead.

Ferro-chrome.	Weight of Sample Taken. Gram.	Weight of Red Lead Used. Grams.	Per cent Carbon Found.
Sample A	1	2	7.26
"	1	3	7.54
"	1	4	7.72
"	$\frac{1}{2}$	3	7.73
Sample B	$\frac{1}{2}$	$2\frac{1}{2}$	7.03
"	$\frac{1}{2}$	4	7.00
Sample C	$\frac{1}{2}$	$2\frac{1}{2}$	6.46
"	$\frac{1}{2}$	$3\frac{1}{2}$	6.55
Sample D	1	1	6.05
"	$1\frac{1}{2}$	$\frac{3}{4}$	5.17
"	1	2	6.403
"	1	4	7.094
"	1	3	7.15
Sample E	1	4	7.07
"	$\frac{1}{2}$	4	7.18

In February, 1906, the copper oxide was omitted from one combustion tube. The space ordinarily occupied with copper oxide was filled, loosely, with ignited asbestos. The following results indicate that the use of copper oxide in combustions with red lead is unnecessary:

Sample.	With Copper Oxide. Per cent Carbon.	Without Copper Oxide. Per cent Carbon.
3 square steel	1.479	1.477
No. 288	1.175	1.175
6 S	0.207	0.207
No. 1193	0.712	0.692
No. 7013	0.520	0.538
C No. 2	1.48	1.51
No. 2703	0.316	0.309
No. 385	0.425	0.439
No. 7014	0.396	0.393
No. 7013	0.401	0.397
No. 1241	0.75	0.765
C No. 3	1.281	1.283
No. 7015	0.409	0.407
No. 7016	0.481	0.478
No. 7017	0.312	0.315
No. 7018	0.425	0.43
No. 7020	0.431	0.431
No. 1200	0.73	0.75
Ferro-manganese	6.31	6.39
Mixture of plumbago and clay	45.96	46.04
Pig iron " B "	3.61	3.58

A red hot body of copper oxide hastens breakage of porcelain tubes by causing unequal cooling strains when the furnace flames are lowered or extinguished for any reason. Since February one tube has been in use without copper oxide. The oxide is still retained in the companion tube, so that daily comparisons have been made.

Since writing this article the author has tried litharge as a substitute for red lead and has found that it possesses some advantages over the latter, being less destructive of boats and tubes. It is in general more pleasant to handle.

Two grams of litharge to the same weight of steel are sufficient where siftings of 20–60 mesh, or thin drillings that can be packed in a close mass, are obtainable. It is extremely rare that such a sample cannot be gotten if the chemist will only insist that a piece of the steel be sent to him instead of drillings that frequently are coated with a film of grease, or contain bits of paper, fine fibers of wool waste, leaf tobacco, blue steel, rust, scale, or clay. He can then take his own drillings with the proper absence of variety. Most chemists are aware that the center of the cross section of a square bar or round piece of steel often contains as much as 50 per cent more phosphorus, sulphur, and carbon than the outside part. Further, that sheet steel just as often varies as much in these elements, and *in spots:* Hence, to get an average and fair sample, a square bar or a round one should be drilled from the surface toward the inside, either half way or all of the way through the sample when practicable.

If for any reason the steel must be drilled on end then a row of holes of EQUAL depth should be drilled all of the way across the section and all of the drilling mixed together. In like manner a flat bar or sheet should have a series of holes of the same depth drilled across it from edge to edge. A failure to observe these precautions often results in disputes between buyer and seller.

It is surprising from what small and hopeless looking pieces of steel one can extract enough drillings of the proper cross section for direct combustion analysis with a good assortment of small drills and a little experience.

For sampling thin sheet steel such as razor blades, and for wire the author has a milling attachment on the drill press table. Milling cutters of $\frac{1}{8}''$ tooth, $\frac{5}{8}''$ stub, and $1\frac{1}{4}''$ diameter are very convenient for taking finely divided millings for direct combustions. In this way either millings or drillings can be obtained on the same table.

CHAPTER XI.

Part II.

THE DETERMINATION OF CARBON IN STEEL, FERRO-ALLOYS, AND PLUMBAGO BY MEANS OF AN ELECTRIC COMBUSTION FURNACE.*

SEVERAL months ago it occurred to the writer that a special resistance wire could be applied to the heating of combustion tubes. A drawing was prepared for a furnace of a muffle type to heat four tubes lying in the same plane and parallel.

After some correspondence it was agreed, at first, to try a single-tube furnace. It consists of a steel tube 295 mm. ×
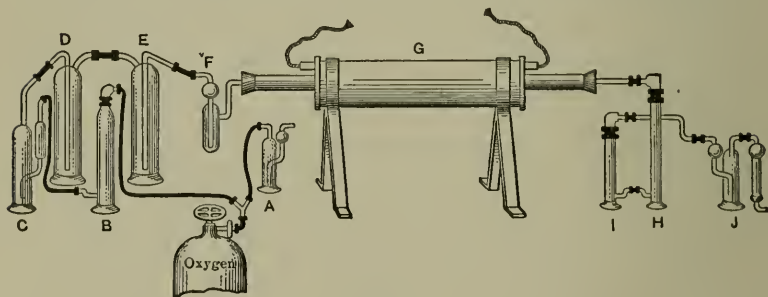
Fig. 5.

76.3 mm. containing a non-conducting packing of magnesia oxide. In the center is a quartz tube wound with the patent wire.† Inside of this tube is placed another of the

* [Reprinted from the Journal of The American Chemical Society (with additions), Vol. XXX. No. 5. May, 1908.]

† Some chemists wind the quartz tubes with platinum ribbon, but the cost is greater. The writer gets three months' service, running night and day, with a reasonable charge for rewiring.

same material of 19 mm. inside diameter and 600 mm. long, in which the combustions are made.

A. Mercury pressure gauge for detection of leaks and stoppages.
B. Jar for stick potassium hydroxide or for any solid drier or absorbent.
C. Safety jar for potassium hydroxide solution, preventing solution from backing over into rubber tubing.
D. Calcium chloride jar.
E. Soda lime jar.
F. Mercury valve, to prevent reverse action.
G. Electric combustion furnace.
H. Jar for granular zinc to remove
   Acid fumes,
   Litharge fumes,
   Sulphur fumes,
   Chlorine fumes.
I. Jar for phosphoric anhydride to remove water.
J. Absorbent and weighing apparatus for carbon dioxide.

The writer put in a small 32-ohm rheostat that happened to be at hand. With about one-fourth of this resistance the furnace, on a 220-volt direct current, has been maintaining a constant temperature. To secure complete combustion of steel, it is very essential that the heat be maintained as close to 950° as possible, i.e., as little under that temperature as practicable. If the temperature drops to about 900° or under, the results obtained are liable to be from 0.01 to 0.10 per cent too low, unless red lead is mixed with the drillings. Hence, if one desires to operate with oxygen alone, the necessity of keeping the temperature from 940° to 960° centigrade cannot be made too emphatic.

The oxygen is purified by passage through jars of stick caustic potash, potassium hydroxide solution, calcium chloride, and soda lime in the order named. The oxygen then passes through a mercury valve into the porcelain or quartz (fused silica) tube, half of which is filled loosely with ignited asbestos. The products of the combustion

are purified from acid, sulphur, litharge, or chlorine fumes
by passing through a jar of granulated 30-mesh zinc.   The
water is removed by a jar of phosphoric anhydride.

For steels containing 0.30 to 1.50 per cent carbon two
grams of fine drillings, not over one-fourth mm. thick,
are taken.   For still lower percentages of carbon 3.0 to
5.0 grams of drillings of not over 20-mesh size are
selected.

The sample is weighed into a clay boat.   (The boat is
molded and burned in the laboratory by a boy at a trifling
cost.)   The steel begins to burn by the time the stopper of
the combustion tube is in place.   Two grams of steel are
decarbonized in three minutes and five grams in six min-
utes.   The burning is continued for ten minutes more with
oxygen passing through the combustion tube at a rapid
rate.   The weighing apparatus is detached, wiped, and
weighed.   Twenty-five minutes afford ample time for a
single combustion, counting all operations.

The weighing apparatus and the jars for the purifying
train are the writer's design, and were first published, in
part, with illustrations, in the January *Journal of the Engi-
neers' Society of Western Pennsylvania*, 1906, and more
fully in the *Journal*, Am. Chem. Soc. **28**, 862 (1906).   This
weighing apparatus (J) is used forty times before it is
refilled.   As it is always weighed against a duplicate for a
tare, after the fortieth combustion its tare is used as an
absorber for forty more combustions, so that when a
pair has been freshly filled the operator knows he can
complete eighty combustions before he needs to refill his
weighing outfit.

While no red lead is necessary for steel combustions, some
of the alloys such as ferro-chrome, carbonless chrome, and
ferro-boron, require that red lead * be mixed with the drill-
ings or powder to break the metallic bond and permit of

* Or litharge.

decarbonization.   Ferro-chrome is the most refractory, as
from a carbon content of more than 4 per cent only 0.2 per
cent was obtained by burning as in steels with oxygen
alone, at a temperature of 940°.   Pig-iron also requires
some red lead.   In general, about one-half the amount of
lead required for decarbonization in a gas furnace is suffi-
cient for the same work in the electric furnace, by reason of
the higher heat attainable within the range of durability.
A few of the many comparisons made in this laboratory
between the combustions in a gas furnace with red lead
and oxygen and combustion in oxygen alone are given in
Table I:

Sample.	Method.	Weight of Drillings Taken.	Amount of Red Lead Used.	Per cent Carbon Found.
		Grams.		
No. 1 Steel............	Electric	4	None	0.09
" 1 "	Red lead .	4	7 grams	0.09
" 288 "	Electric	2	None	1.176
" 288 "	Red lead	2	4 grams	1.175
" 2 "	Electric	5	None	0.121
" 2 "	Red lead	4	7 grams	0.111
" 3 "	Electric	1½	None	0.976
" 3 "	Red lead	1½	4 grams	0.967
" 4 "	Electric	3	None	0.109
" 4 "	Red lead	5	7 grams	0.118
" 5 "	Electric	2	None	0.469
" 5 "	Red lead	2	4 grams	0.474
" 6 "	Electric	2	None	0.736
" 6 "	Red lead	2	4 grams	0.737
" 7 "	Electric	3	None	0.118
" 7 "	Red lead	4	7 grams	0.117
" 8 "	Electric	2	None	1.17
" 8 "	Red lead	2	4 grams	1.168
" 9 "	Electric	2	None	1.15
" 9 "	Red lead	2	4 grams	1.16
" 10 "	Electric	5	None	0.046
" 10 "	Red lead	4	7 grams	0.040

FERRO-ALLOYS AND PLUMBAGO.

Sample.	Method.	Weight of Drillings Taken.	Amount of Red Lead Used.	Per cent Carbon Found.
		Grams.		
Tungsten powder........	Electric	2	None	0.003
	Red lead	2	4 grams	0.010
Plumbago, No. 153.......	Electric	0.3	None	50.700
	Red lead	0.2	4 grams	50.800
Plumbago, No. 356.......	Electric	0.3	None	51.650
	Red lead	0.2	4 grams	51.300
Plumbago, No. 1.........	Electric	0.2	None	94.900
	Red lead	0.3	4 grams	94.300
68.5% ferro-chrome......	Electric	1.0	1 gram	4.21
	Red lead	1.0	4 grams	4.15
Ferro-vanadium, No. 134.	Electric	1.0	None	3.12
	Red lead	1.0	4 grams	3.09
Ferro-titanium, No. 1	Electric	2.0	None	0.22
	Red lead	2.0	4 grams	0.24
Ferro-boron, No. 1.......	Electric	1.0	1 gram	1.73
	Red lead	1.0	4 grams	1.72
{ Carbonless chrome, No. 9	Electric	1.0	1 gram	0.08
{ 96.0% chromium	Red lead	1.0	4 grams	0.09
Pig iron................	Electric	1.0	None	3.20
"B"	Electric	1.0	0.5 gram	3.58
	Red lead	1.0	4 grams	3.58

The advantages of the electric heating apparatus are obvious. Very little heat is radiated; economy of space is attained; tubes are heated gradually and cooled gradually; time required is the minimum; labor cost is plainly the lowest because of simplicity and rapidity, and no expensive platinum tubes or boats or crucibles are used.

Some may say, "Why not burn the steel in air?" The answer is that the cost of oxygen is small, one-third cent per combustion, and the steel burns twice as fast. Oxygen can now be had at 5 cents per cubic foot in 100 cubic foot cylinders. The method is accurate for all steels. As pointed out in the writer's article and in his preliminary paper read before the Pittsburg Section in December, 1905, one may lose as much as 50 per cent of

the carbon in certain alloy steels by attempting to dissolve
the borings in either neutral or acid double chloride of cop-
per and potassium.

The best protection for the bottoms of clay or porcelain
boats is a liberal layer of ignited silica sand, such as is used
for acid open-hearth furnace bottoms.   The silica rock is
crushed to about 20-mesh and ignited in a muffle furnace
at a bright red-heat, cooled, and kept in glass-stoppered
bottles.   Test the sand by a blank analysis.

To secure complete decarbonization it is necessary either
that thin drillings be used, or if the sample contains much
coarse or bulky material, it should be selected.   This can
easily be accomplished by pouring the borings on a 20-mesh
sieve and shaking all of the steel of 20-mesh size and the
still more finely divided dust on to a 60-mesh sieve, which
retains only the 20 to 60-mesh material.   This *always*
represents a good average sample.

Further, the drillings should be placed in as compact a
mass as possible.   If curly drillings are scattered along
the entire length of the boat instead of being put in a deep,
compact body, borings that are a little thick will frequently
be found to still contain unburned metal.   This detail is
a very important one.   Of course, the reason is that drill-
ings lying in close contact heat each other to incandescence
during the burning with oxygen.

Also, during the period when the oxygen is being ab-
sorbed in large quantity by the burning metal, the flow
of the gas should be regulated so that there is an
excess.   That is, the oxygen must be turned on in suffi-
cient quantity so that the gas is bubbling through the
weighing apparatus slowly.*   However, if the gas is rushed

* In order to maintain the slow bubbling through (*J*), it is necessary to
increase considerably the rate at which the oxygen is passing through
(*C*) during actual burning of the metal to oxide.   This also generates
the required white heat in the steel at the critical time.

through (J) during this period the steel becomes violently heated and slags with the sand and the sides of the boat, destroying the latter. Worse yet, low results are obtained frequently in this way, probably due to the formation of carbon monoxide, which is driven out of the hot portion of the tube before it is oxidized to the dioxide.

If the oxygen is turned into the tubes in sufficient quantity to maintain a slow stream during the period of the burning, the end point of the combustion is distinctly shown by a sudden increase of the speed of the bubbling through (J). The rush of oxygen is then checked, but the rate of flow is still rather rapid for the final ten minutes.

The weighing apparatus (J) is filled not quite to the bend of the inlet tube with a solution of potassium hydroxide made by dissolving 500 grams of the latter in 500 c.c. of water. The drying tube at the outlet of (J) is closely filled with pieces of stick caustic potash cracked to about half the size of a grain of wheat. To prevent the caustic potash from coming in contact with the small rubber stopper in the drying tube a *loose* plug of asbestos is placed at that point. The little bulb of this drying tube is filled about half full of glass wool. If dry sticks of caustic potash are cracked quickly, the small pieces can be conveyed to the drying tube in dry condition and constitute not only a splendid guard against loss of moisture from (J) but are also equally effective as an absorbent of carbon dioxide.

If a porcelain boat is used, the 15 × 75 mm. Royal Meissen boat is the best shape and most durable of any porcelain boats that the writer has tried. When putting in the sand bottom, fill the front half of the boat about two-thirds full and then with the butt end of the forceps make a trough in the sand, working it well up the sides of the boat. Pour the drillings from the weighing bottle into this depression. By so doing the drillings are kept in a compact mass, and when the combustion is completed the

burned steel can be lifted out in a small cake.   In this way a boat can be used ten to fifteen times.

When a great many combustions are made daily, the fused silica, or electro quartz, tube is the most serviceable. The continuous spraying of oxides against the walls of a porcelain tube weakens it, and when the current is turned off and the tube is permitted to get cold the contraction causes a rupture.   Avoid spilling steel in a quartz tube.

To prevent the contents of D, B, E from clogging the inlets and outlets, large plugs of cotton are used at these points.   Glass wool plugs should be used in H and loose plugs of ignited asbestos in I.   Enough mercury is placed in the bottom of F and A to form a seal.   The inlet end of the quartz tube heats somewhat, and it is better to wrap it several times around with a strip of cheese-cloth, the end of which dips into a 150 c.c. beaker of water suspended directly underneath by means of copper wire.   During the absorption of carbon dioxide the outlet of J is protected from ingress of moisture or carbon dioxide or fumes from the room by a drying tube not shown in the figure.   It is filled with pieces of stick caustic potash broken to the size of a pea.

Oxygen can now be had, under high pressure, in 50-foot cylinders at about 5 cents per cubic foot, and in 100-foot containers at about 4 cents per foot.   The latter quantity will supply two furnaces, night and day, for two months.

Gas Combustion Furnace with Blast.   The gas combustion furnace described by the leading supply houses as " for draft or blast; with adjustable flame length " can be made very effective where compressed air is at hand. The author modifies it as follows: From the 450 mm. size take out one pair of tiles; shove the other two pair together into the middle of the furnace frame.   Put the removed tiles on top of the remaining four to lessen radiation of heat.   Close all of the burner shutters except the

four middle ones. Let the inlet end of the $\frac{3}{4}''$ inside diameter, 30″ electro-quartz tube project 12″ beyond the tiles, and the outlet end 6″ beyond the tiles. Fill the latter end, *loosely*, with ignited asbestos for a distance of 8″, beginning at the stopper. Wrap both ends at the stoppers with wet cheese-cloth as in the electric furnace. It is essential that the combustion tube be at least 30″ long, and either of electro quartz or platinum, as with air blast and gas the furnace will heat the tube to 1150°– 1200° C. in twenty minutes! This is in the range of temperature where it is possible to make direct combustions with air passing through the combustion tube instead of oxygen. Of course such a furnace is noisy and radiates quite a little heat, but is inexpensive.

In addition to the wet wrappings, with such extreme heat, it is safer, after putting in the charged boat, to follow it with a loose plug of ignited asbestos, placed in the tube about an inch beyond the inlet end. This protects the stopper entirely from radiated heat. This plug can be used over again.

At 1000° C., using oxygen, coarser drillings can be decarbonized than at 950° C., and more quickly. Clay boats will not stand 1100° C. They crumble. Porcelain ones flux with the steel. Platinum boats are necessary at 1100° C.

When making combustions with air instead of oxygen, it is advisable to pass the gases formed through a second tube filled with copper oxide or some other catalyzer heated to redness. Do not put oxide of copper in a quartz tube. It will flux it. A $\frac{5}{8}''$ bore R. B. porcelain tube, 14″ long, heated by a 5-burner Bunsen combustion furnace answers very well. With such a catalyzer direct combustion of steel drillings, in air, is successful at about 1150° C.

CHAPTER XII.

CARBON BY COLOR.

THE determination of carbon by color methods should be indulged in as little as possible. Numerous interferences render analyses, unless carried out under the guidance of persons of long experience, highly inaccurate. The heat treatment, i.e., the greater or less amount of *incidental* annealing that a sample may have had, will cause the color to vary, yielding results 10 per cent to 20 per cent away from the actual carbon. The perfectly annealed steel, i.e., where the carbon has all been converted into the absolutely annealed condition, yields the greatest depth of color for a given percentage. A few tenths of a per cent of highly coloring elements like chromium give low results compared with a standard steel not containing the alloy. Also the presence of considerable manganese tends to lighten the color in unannealed steel. The same is true of nickel.

If a sample consisting of large, bulky, thick drillings be compared with a standard of small, uniform size, thin drillings, the bulky sample will yield results often 10 per cent too low. The presence of graphitic carbon will cause results to be anywhere from 5 per cent to 90 per cent too low. Of course, much graphitic carbon is easily detected by the insoluble black residue that remains in the solution so that only 5 per cent too low is likely to be unnoticed. A practiced eye will detect the slightest trace of it. If the operator can drill his own samples and always get them

with the same heat treatment, and have a standard that has undergone the same treatment, and has been drilled with the same depth of cut, his results will be fairly accurate.

There are two means by which one may approach the above ideal:

First. When the drillings to be tested and the standard drillings have been taken from the raw cast steel that has never been reheated and is always allowed to cool slowly from the molten state, i.e., without any quenching.*

Second. Where the operator is furnished the steel and can anneal it to the last degree of softness, avoiding the temperature range most favorable to the formation of graphitic carbon (see Annealing of Steel). Then drill such samples to uniform thickness and compare them with a standard prepared in exactly the same manner. This second scheme is the most accurate of all color methods. For the identification of the perfectly annealed condition, see Annealing.

Further, it is essential in color work that the standard shall be within 10 per cent of the carbon content of the sample to be tested. The nearer the carbon of the standard is to that of the test, the better; especially is this true of unannealed steel.

Method. Dissolve 100 milligrams of sample in 4 c.c. of 1.20 nitric acid. Use a test tube 152 mm. × 15–16 mm. diameter. Insist that the dealer supply test tubes that keep within the same diameter. If one test tube is wide and its mate narrow, the wide one will permit more of the free acid to escape than the narrow one, causing variation in the color. Do not set the tubes deep in the boiling water, as it will cause iron to dry on the sides, and, when this is redissolved by shaking the hot acid solution the brown basic nitrate of iron will go into solution, causing another variation of color. The fewer tests dissolved at one time the better, as some parts of the bath will be

* Quenching can be safely done provided the test piece is first cooled to a black heat in an entirely dark closet.

hotter than others, causing more loss of acid from the tubes in the hotter location. In forty minutes all of the flakes of carbon are usually dissolved on a water bath. These baths are designed especially for this work, and contain racks to hold thirty-six tubes. · These racks have false bottoms perforated with many small holes. This arrangement permits the tubes to be immersed to the depth of 28 mm., which is about the level of the nitric acid.

For more rapid solution of the carbon, requiring four to seven minutes, use a sand or graphite bath heated to about 190° C. Plunge the tubes into the bath just to the top level of the acid in them. Keep the tubes close together and do not run more than six tubes at a time, as such a bath is liable to great variation in temperature. The writer collects a set of six tubes in a compact cluster and covers all with a 5-ounce beaker. This prevents too rapid loss of acid. Remove the tests the second that the brown flakes are in solution. Use standards within 5 "points" (0.05 per cent carbon) of the tests so that tests and standards will go into solution at about the same moment.

The tests are quickly cooled in running water and compared in the bent-end comparison tubes, which permit the contents of the tubes to be mixed by a rocking motion. The comparison tubes are of 14 c.c. capacity, and graduated to tenths of a c.c. The length of the graduated portion is 181 mm. Then follows 45 mm. of ungraduated tube. Then the part bent at an obtuse angle. The bent limb is about 50 mm. long. The outside diameter of the tube is 12 mm. A set of three of these tubes is used. The specifications for these tubes should require that all three tubes be the same inside and outside diameter throughout their graduated portion. The figures and graduation lines should be small, the figures not over 2 mm. long and the lines not over 4 mm. long for c.c., and not over $1\frac{1}{2}$ mm. long for tenths of a cubic centimeter.

The graduations of all three tubes should coincide with each other. For example, the 14 c.c. mark should be exactly the same distance from the bottom of the comparison tube in each tube of a set, thus proving that the inside diameter is uniform throughout the set.

The tubes should be free of fine black lines due to bubbles in the glass when it was drawn into tubing.

The tubes should be made of selected tubing free of scratches. The graduations should be as exact as those of a burette.

All color carbons should be made in duplicate and results averaged. Nothing is gained by operating on a greater amount than 0.100 gram. The writer, in his practice, ran a great many color tests, using 0.500 gram, and found the same lack of agreement, and much more acid is needed.

The Comparison. If, for example, a 0.60 carbon standard is in use pour it into the comparison tube, using as little rinse water as possible, so that the volume of the fluid in the tube is just 6 c.c.; mix thoroughly.

The test is then put in another tube, and water is added to it until its color is the same shade as that of the standard, mixing carefully with each addition of water. This matching should be conducted slowly when the test is still but slightly darker than the standard. But two-tenths of a cubic centimeter should be added at a time when the test is only slightly darker than the standard, so that when the former is finally very slightly lighter than the standard, the operator knows he has overstepped the end point 0.01 per cent, which he deducts from the reading. If the test, for example, is just turned lighter at 6.5 c.c., then the per cent carbon will be 0.65 less 0.01 or 0.64 per cent carbon. If a standard of 0.30 carbon is in use, it is diluted to 9.0 c.c. Should the test match it at 6.0 c.c., then the carbon percentage will be 0.60 ÷ 3, or 0.20 per cent carbon. If a standard of 0.40 carbon is used, it is diluted to 8.0 c.c. If the test matches it at 7.0 c.c., for example, then the per cent

carbon will be $0.70 \div 2$, or 0.35 per cent carbon.   If a standard of 0.08 per cent carbon is in use, it is diluted to 5.6 c.c. Should the test match it at 6.0 c.c., for example, the per cent carbon would be $0.60 \div 7$, or $0.085 =$ per cent carbon. When a large number of color tests must be made, they should be checked at frequent intervals by combustion; for instance, if a lot of 30 color tests are made, and every fifth one is checked by combustion and checks within $0.01 - 0.03$ per cent in a range from 0.50 per cent and over, it is pretty safe to assume that that particular lot of color tests was done under favorable conditions.

The writer does not use a comparison camera, but decidedly prefers to hold the tubes on a sheet of white paper in diffused sunlight.   The direct glare of the sun is, of course, undesirable.

At night a 50-candlepower frosted electric lamp of filament type resting on a sheet of white paper from a flexible arm is the best source of light.   The comparison tubes should be held * with the graduations touching each other, thus giving a clear field of color.   Their relative right and left positions should be changed at intervals of a few seconds to assist the operator in judging respective depths of color.   He should endeavor to lose track of which is test and which is standard, and if, under such conditions, he finds he can come to the same conclusion three times in succession, then he is as certain as possible of his choice of the light one and the dark one.   In the writer's opinion the least source of error in carbon color work is the operator's eye.   A man with a good eye for color and plenty of practice can be counted on not to introduce an error due to the eye of over 0.02 per cent in higher carbons and of not over 0.010 per cent in lower carbons, around 0.08 and perhaps not over 0.005 per cent in the latter range.

Reject all drillings that are blued, or rusty.

* The comparison tubes should be held at an angle of about 45° to the paper with their ends touching the same.

CHAPTER XII.

Part II.

VOLUMETRIC PHOSPHORUS IN PIG IRON, STEEL, WASHED METAL AND MUCK BAR.*

Dissolve 1.63 grams of sample in 45 c.c. 1.13 nitric acid, using a 5 ounce beaker. Heat gently on hot plate or bath of some description. The writer uses a twelve-hole affair as shown in Fig. 1. Highly silicious pig iron dissolves slowly
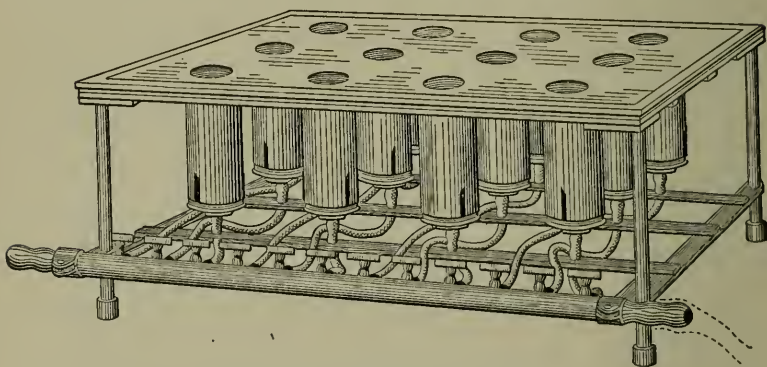
Fig. 1. — Phosphorus in steel.

and it is best to maintain all pig iron samples at digesting heat (barely boiling) for at least twenty minutes. To assist in dissolving pig iron add four drops of hydrofluoric acid to the solution after it has been digested ten minutes with the nitric acid, if high silicon is suspected.

* Hundeshagen (modified by J. O. Handy) first recommended the titration of the yellow precipitate by standard alkali.

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For pig iron and some chrome steels the next step is to filter out the insoluble graphite, etc. Wash the residue on the filter fifteen times with the dilute nitric acid wash. All phosphorus filtrations in this laboratory are made on a revolving filter stand. (See Fig. 2.)
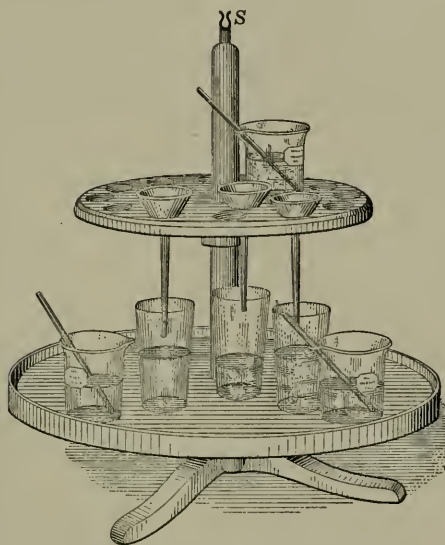
FIG. 2.— Phosphorus in steel.

It is not necessary to filter solutions in plain carbon steels. Filter the muck bar solutions if they contain much insoluble residue.

Add to the filtered solutions of pig iron, chrome steel, and muck iron and to the unfiltered solutions of plain steel and washed metal, from a convenient drop bottle, the potassium permanganate solution. Continue the addition of permanganate until the excess of manganese separates as a brown precipitate that does not disappear noticeably after 10 minutes, boiling. As washed metal usually contains about 3.00 per cent of carbon it will consume considerably more

of the permanganate solution before the carbon is destroyed than ordinary steel. The excess of manganese precipitate is removed by adding ferrous sulphate solution, free of phosphorus, from a dropper until the solution is again clear.
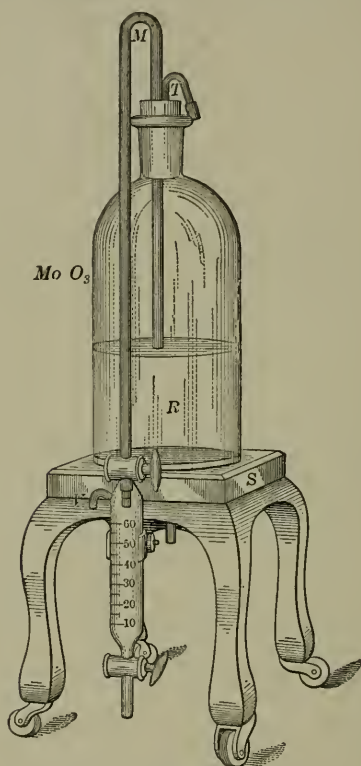
Fig. 3.— Phosphorus in steel.

After five minutes more boiling the beakers are removed from the fire, the covers are rinsed off and the inside walls of the beakers are washed (to prevent the phospho-molybdate sticking to the walls) down, 50 c.c. of the special phospho-molybdate are run into each test from a measuring siphon. (See Fig. 3.) A batch of 12 tests are

stirred at a time, using glass rods. A single test is stirred around twice, then the next one, and so on until each test in the lot has been stirred ten times. This means that each solution has been stirred at intervals during a period of ten minutes. The twelve samples are put on the revolving stand and twelve 7 cm. filters are marked with a lead pencil to correspond to the respective tests. The only interval between the completion of the stirring and commencement of the filtration is the time required to fit the filter papers to the funnels.

The liquid is decanted through its proper filter and the bulk of the precipitate is allowed to remain in the beaker until the filter papers are washed ten times, giving each paper a washing, then the next one and so on until number one is reached again. By the time number one is ready for its second washing, the first washing will be well drained off. Each funnel stem is given a turn with the thumb and forefinger in such a manner that the double fold of the paper is washed twice and the single fold once during each washing. Use the dilute nitric acid wash.

Ten washings having been accomplished, the main body of the yellow precipitate is washed on to its respective filter with a fine jet of the acid wash, and receives a further ten washings to remove iron.

To remove free acid the precipitates are next washed thirty times with the potassium nitrate water. The filters are now removed to a large watch glass. A ruled slip is dated and headed and the various tests are entered thereon. On the right-hand side is kept a record of the alkali used, and on the left, the acid standard used in the subsequent titration of the yellow precipitate.

The titration is accomplished by placing filter and precipitate in a 100 c.c. beaker. The standard sodium hydroxide solution, 1 c.c. of which equals 0.01 per cent phosphorus when 1.63 grams are taken, is dropped on the filter until

the yellow precipitate has dissolved.* Then add 50 c.c.
distilled water. Two drops of phenolphthaleine are intro-
duced, and from a second 50 c.c. burette standard nitric
acid is run into the rose-colored solution until one drop of
acid discharges this color. The total number of c.c. of
alkali added, less the number of c.c. of acid required to
discharge the rose color, multiplied by 0.01, gives the per-
centage of phosphorus in the sample.†

GRAVIMETRIC PHOSPHORUS.

If it is desired to check the volumetric method by weigh-
ing the yellow precipitate, proceed exactly as given under
the latter process, with the following exceptions:

First. Filter *all* solutions as in pig iron.

Second. Omit the washing with potassium nitrate and
use only the dilute nitric wash to remove iron, leaving the
acid in the filter paper.

Third. Filter the yellow precipitate on 7 cm. ashless
filters that have been previously weighed hot between
watch glasses with edges ground to fit water-tight when held
firmly together, nearly full of water, in a vertical position.

These filters are weighed as rapidly as possible after hav-
ing been dried at temperature of boiling water. The phos-
pho-molybdate is collected on the weighed filters and
washed free from iron with the dilute nitric acid. The
filters are again dried as before, for one hour, and weighed.
The weight of the filter paper plus the dried precipitate, less
the weight of the paper, less the blank (obtained by filtering
a clear filtrate from some previous phosphorus determina-
tion through a weighed paper, washing it, drying it and re-
weighing it as in an actual analysis) equals the percentage
in the sample when 1.63 grams are used for analysis. This

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* It is safer to add, at least, 1 or 2 c.c. excess of the alkali standard.

† Figs. 1, 2, and 3 were designed some years ago by Dr. Edward S.
Johnson.

method is valuable only as a check, as too much time is consumed.

In both methods the filtrates and washings are placed on a shelf for one hour. If a cloudy ring forms at the junction of the washings and the main body of the filtrate, results will be too low. If the cloud gradually spreads, the results may be as much too low as 0.01 per cent in a possible 0.100 per cent.

After considerable practice one can estimate with sufficient accuracy for most mill control, all phosphorus 0.02 per cent and under by simply examining the yellow precipitate after it has had an opportunity to settle for about twenty minutes in the 5-ounce beaker. The prevention of cloudy filtrates will be discussed under the heading "*Molybdate Solution.*"

Standard Sodium Hydroxide Solution.

One hundred and fifty grams of sodium hydroxide and one gram of barium hydroxide are dissolved in 1000 c.c. of water. Let the solution stand for two days. Siphon off the fluid and dilute it to two liters. Dilute 275 c.c. of this stock solution to 3500 c.c. On testing, suppose it is found that 20 c.c. of the alkali standard equal 20.75 c.c. of the acid standard. This gives the proportion 20 : 20.75 : : 3400 : x (= 3527.) Therefore dilute the remaining 3400 c.c. to 3527 c.c. when 20 c.c. of the NaOH standard will equal 20 c.c. of the standard acid or 1 c.c. NaOH = 0.010 per cent phosphorus when 1.63 grams of sample are used for analysis. It is always best to confirm this value by running several steels whose phosphorus content is accurately known.

Standard Nitric Acid.

Dilute 74 c.c. 1.20 nitric acid to 3500 c.c. On titrating with standard NaOH, suppose it is found that 19.2 c.c.

of the acid equal 20 c.c. of the alkali: 19.2 c.c. : 20 c.c.
: : 3400 : x (= 3541). Therefore the remaining 3400 c.c.
are diluted to 3541 c.c. when 20 c.c. of standard acid should
equal 20 c.c. of standard alkali.

For preparation of 1.20 specific gravity nitric acid from
concentrated acid see Chapter XV.

MOLYBDATE SOLUTION.

Dissolve 183 grams of unignited molybdic acid plus 2
grams of ignited (melted) molybdic acid in 900 c.c. of
11.50 per cent ammonia water plus 250 c.c. of distilled
water. Cool this solution and add it a little at a time to
2700 c.c. 1.20 nitric acid. Cool the nitric acid after each
addition of the molybdate. If the nitric acid is allowed to
get too greatly heated the molybdic salt will precipitate in
large quantity. Add to the solution 0.5 gram of sodium
ammonium phosphate and filter it through a pulp filter
(using suction) after twelve hours' standing.

Some years ago the writer observed that a solution of
ammonium molybdate in nitric acid, made as here given,
will produce different varieties of the yellow precipitate.
Other conditions being unchanged, an ammonia solution
of molybdic acid prepared from ignited, i.e., crystalline
anhydrous molybdic acid, causes the yellow precipitate to
separate from the nitric acid solution of the steel in an
extremely fine state of division. Such a precipitate will
remain suspended in the solution for hours without sub-
siding and will run through a filter paper almost as though
it were a solution instead of a precipitate. This precipitate
has only one redeeming feature: It is the least soluble in
the dilute nitric wash of any of the varieties of ammonium
phospho-molybdate that are encountered under the con-
ditions that are cited here. Now if no ignited molybdic
acid is used in the preparation of the molybdate solution,
the phospho-molybdate settles rapidly and does not run

through a filter. But this variety has the objection that it is the most soluble form of phospho-molybdate, in nitric acid. This variety of precipitate will leave the filtrate perfectly clear, but after the latter has stood for an hour (if much precipitate has dissolved in the wash water) or perhaps not until the next day (if little of the yellow precipitate has dissolved in the dilute nitric wash) a milky ring of phospho-molybdate will appear at about the point where the washings lie on top of the main body of the filtrate. If much of the yellow precipitate has been dissolved, say about 1/10 or 1/20 of its weight, this cloud will spread through the entire filtrate.

The ideal yellow precipitate is that one whose physical condition is such that it will give a clear filtrate and be practically insoluble in the wash. The author has had brands of molybdic acid that require equal weights of the crystalline molybdic acid and of the unignited variety to produce the desired results. At present but two grams of the crystalline material are needed for the particular brand of molybdic acid now in use.

To prepare crystalline molybdic acid the author melts in a porcelain dish the ammonia-free, so-called c.p., molybdic acid which melts rapidly at a bright red-heat to a clear fluid, and, on cooling, forms handsome crystals that can be readily reduced to a powder in a porcelain mortar.

POTASSIUM PERMANGANATE SOLUTION FOR OXIDATION OF THE CARBON.

Fifty grams of the salt dissolved in one liter of water.

FERROUS SULPHATE SOLUTION.

Two hundred and fifty grams of the phosphorus-free salt dissolved in 1000 c.c. of water acidulated with 20 c.c. 1 : 3 sulphuric acid.

Dilute Nitric Acid Wash.

Two hundred and thirty c.c. 1.20 nitric acid diluted with 8100 c.c. of water.

Potassium Nitrate Wash.

Dissolve 50 grams of potassium nitrate in 2500 c.c. of water for a stock solution.

Dilute 700 c.c. of the latter with 7000 c.c. of water to constitute the wash.

Phenolphthaleine Indicator.

One gram of this substance is dissolved in 100 c.c. of absolute alcohol.*

* See remarks at the close of Chapter XI, Part I, on the proper way to drill a steel sample in order to obtain borings that represent the average of the piece in phosphorus, sulphur, silicon and carbon.

CHAPTER XII.

SULPHUR IN STEEL, MUCK BAR, PIG IRON AND WASHED METAL.

VOLUMETRIC.

DISSOLVE three grams of sample in 70 c.c. of 1 : 1 hydrochloric acid. More than this amount of acid is sometimes required for rapid solution. The dissolving flask is the author's design and is made in a mold with a fire finish, ring neck. The flask, being made in a mold instead of by hand, has a perfectly round neck and always takes a No. 6 rubber stopper. Its capacity is 275 c.c. to base of neck, and its height is 165 mm. It is a great convenience to have these details always the same. (Fig. 4.) Previous to designing this flask much trouble was experienced in different lots of flasks. In the same lot some would require a No. 4, others a No. 5, and some a No. 6 stopper to get a good fit. Then ground finish flasks will crack at the neck when placed in the heater to dry out the water.

FIG. 4.

Drillings are never weighed into wet flasks. The No. 6 stopper is perforated with three holes, one to receive a bulb funnel of 75 c.c. capacity. This funnel is also designed to
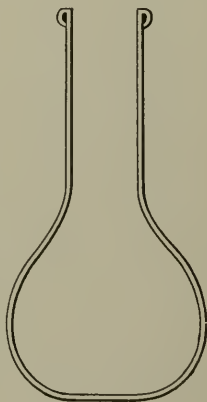
facilitate the work.   It has an opening at the top of the bulb of 15 mm. diameter.   The glass cock has an extra large hole bored in it (3½ mm. diameter) to permit of rapid flow of the acid from the bulb into the flask.   The total distance from the base of the bulb to the outlet in the stem is 145 mm.   The second hole in the stopper admits a small tube that dips just below the level of the fluid in flask.   After the iron is completely dissolved, hydrogen is forced through this inlet for three to five minutes to drive out any hydrogen sulphide that may remain in the interior of the flask.   The third hole admits the delivery tube which carries the evolved gases to the bottom of the absorbing solution of ammoniacal cadmium chloride.   This solution is contained in a thick wall, thick bottom, test tube about 10 inches by 1 inch.   Fifty c.c. of the solution are used for each analysis.

The flask is clamped in a rack supporting four flasks to the stand.   Each stand is supplied with four burners.   The top of the stand on which the bottoms of the flasks rest is an asbestos copper-rimmed board with a circular hole of 42 mm. diameter cut in it immediately over each burner. The bottom of the flask rests in this hole.   Ranged alongside of this rack is a wooden one holding the four absorption tubes.   As many such sets of four are in operation at one time as the chemist can manage.

When the solutions no longer evolve gas to any extent without the aid of heat, the flames are raised slightly so as to maintain a very slight boiling action.   When heat no longer produces gas bubbles in the absorption tubes, the hydrogen is turned in and a rather rapid passage of this gas is continued for three to five minutes.   The cocks on all of the bulb funnels are then opened.   The hydrogen is shut off at each flask.

The cadmium solution containing the precipitate of sulphide is poured on a rapid running No. 597 11 cm. S. & S.

filter. The absorption tube is rinsed with water and the washings are poured on the filter. The latter is washed three or four times with water. The delivery tube, if much precipitate adheres to it, is cleansed by rubbing it with a little filter paper. This small piece of paper is then dropped in on the main portion of the cadmium sulphide to which it belongs. The delivery tube without further washing is put back into its respective absorption tube.

Both tubes together with the filter paper containing the major part of the sulphide are taken to the titration table together with the other tests which have been similarly prepared. The filter paper with the adhering sulphide is placed in a 1000 c.c. beaker containing 500 c.c. of water. For convenience the beaker should have an etched mark on it to indicate the half liter.

The paper is beaten into fragments with a glass rod and the pulp is stirred all through the water. Two c.c. of starch solution are added. The absorption tube corresponding to this filter is filled one-quarter full of distilled water and then to within an inch of the top with 1 : 1 hydrochloric acid. Further, the delivery tube, which has been momentarily removed from the absorption tube previous to adding the water, is returned to the acid fluid, and is raised and lowered in it to dissolve any small quantity of cadmium sulphide adhering to its interior or exterior walls. It is then laid aside and the fluid in the absorption tube is poured into the water containing the bulk of the yellow sulphide. This acid is not dumped in promiscuously but is allowed to run down the inner wall of the beaker rather slowly so as not to disturb the contents thereof. Before stirring the acid through the latter, iodine is dropped in from a Gay-Lussac burette held in the operator's left hand. The drops are added in such a way that a circle of drops extends around the inner circumference of the beaker. With his other hand the operator now gives the solution in

the beaker a *slight* stir with a glass rod.   If this causes the blue to disappear, leaving a reddish tint, another circle of drops of iodine is added, and so on until two or three drops of the standard iodine solution produce a purplish blue end point which does not fade to a red with more stirring.

The number of c.c. of iodine used less the number of c.c. required to produce a faint blue in a blank test, multiplied by the percentage value in sulphur of the iodine standard, equals the per cent of sulphur.   The blank test is made on the same amounts of starch, filter paper and water as are used in an actual analysis.

This sulphur value is obtained by running steels of known sulphur content in the manner described.

The U. S. Bureau of Standards, Washington, D. C., also furnishes phosphorus, sulphur, silicon and manganese standards for pig iron and steel that have been analyzed by chemists experienced in iron and steel analysis.   These constitute a valuable aid to the analyst, enabling him at any time to check his own standards.   The cost of these standards is low.   Steps are being taken with a view to preparing also a series of various alloy steel standards standardized as to vanadium, titanium, chromium, tungsten and molybdenum content.

Each day a standard steel should be run with the other work, as new acids and chemicals are liable to cause the sulphur value of the iodine to change from that originally obtained when it was first standardized.

This method is accurate for all unhardened plain carbon steels, and for annealed pig iron and for muck bar.   In chilled pig iron, unless first annealed, the results are usually about 25 per cent lower than the actual sulphur, and yet, in spite of this fact, by reason of its rapidity, practically, the method as given is very generally in use by buyer and seller of pig iron.   The practice of annealing the drillings

in covered crucibles, at a red heat, for 15 minutes, may probably come into vogue.

However, if the buyer and seller understand the limitations of the method it would seem unnecessary to resort to this detail. The steel furnace superintendent could calculate his sulphur content one-fourth higher than the laboratory report. Or the buyer and the seller could agree that if their respective laboratories find 0.060 per cent sulphur, for example, in pig iron, it shall be reported as 0.075 per cent, thus saving valuable time in the laboratory and have records that are sufficiently close to the truth for all practical purposes.

The evolution method is unreliable for steels high in copper and for many alloy steels that form carbides that are insoluble in 1 : 1 hydrochloric acid. The results are too low. (See analysis of these steels.)

The Starch Solution.

Grind one gram of good wheat starch, free from rancid smell, to a powder. Stir it with 10 c.c. of water in a small beaker and put it carefully into 90 c.c. of boiling water. Cool and use as needed. It is best to prepare this solution daily.

Iodine Standard.*

One gram of best resublimed iodine is dissolved in a very little water together with 10 grams of c.p. potassium iodide. This is diluted to 1000 c.c. with distilled water. It is standardized against a steel of known sulphur content.

Cadmium Chloride Solution.

Twenty grams of anhydrous cadmium chloride are dissolved in 1400 c.c. of ammonia water of 0.9 specific gravity. This solution is diluted to four liters with distilled water for use.

* One c.c. of this standard equals from about 0.0042 to 0.0045% of sulphur when 3 grams of sample are taken for analysis.

Lead Acetate Solution.

For purification of the hydrogen before it enters the sulphur flasks, it is allowed to bubble through a 500 c.c. Bunsen wash bottle containing a solution of lead acetate made as follows: (1) Dissolve 100 grams of lead acetate in 400 c.c. of water. (2) Dissolve 400 grams of potassium hydroxide in 500 c.c. of water. Pour one solution into the other and mix thoroughly. Use 120 c.c. of this solution in each wash bottle.

The hydrogen is generated in an ordinary Kypp apparatus.

Gravimetric Sulphur in Pig Iron, Steel, Washed· Metal, and Muck Bar.

Dissolve five grams of drillings of 0.04 per cent and higher sulphur content in 200 c.c. concentrated nitric acid, using an 800 c.c. beaker. For percentages of sulphur under 0.04 per cent use 10 grams of drillings, dissolving the latter in 300 c.c. of concentrated nitric acid. Add the nitric acid a few c.c. at a time, as the reaction is violent. When all acid is in the beaker, warm the contents of same until action is over. Then add two grams of sodium carbonate. Transfer the solution to a No. 6 dish and evaporate on the sand or graphite bath to dryness. Dissolve in 100 c.c. of 1.20 hydrochloric acid, keeping the dish covered until spraying ceases. Remove the cover and evaporate to dryness again. Dissolve once more with 50 c.c. concentrated HCl and evaporate to a scum. Add 10 c.c. of concentrated hydrochloric acid, or more if necessary, and heat with cover on until all iron is in solution. Add 100 c.c. of water. Filter; wash with dilute HCl (1 : 20). Dilute the filtrate and washings to 400 c.c. Heat to boiling. Add 60 c.c. of a saturated solution of barium chloride, diluted with 200 c.c. of water. Filter the barium chloride before using it. Stir the solution thoroughly after adding the

barium chloride.   After twelve hours, filter the precipitated
barium sulphate on a double 9 cm. ashless filter.   Barium
sulphate is quite soluble, even in very dilute hydrochloric
acid.   It should be washed free from iron with cold water
and only an occasional washing with water containing one
or two drops of 1 : 1 hydrochloric acid in 100 c.c. of dis-
tilled water.

Wash about every fifth time with this acidulated water
until no iron test is obtained with KCNS and then free
from chloride test with water alone.   Ignite in a weighed
platinum crucible.   Add one or two drops of 1 : 3 sulphuric
acid and ignite again.   Weigh as $BaSO_4$.   Obtain a blank
in the same way.   Deduct the $BaSO_4$ found in the blank
and multiply the remainder by 13.73 and divide the prod-
uct by the weight taken for analysis to obtain per cent of
sulphur.   If the barium sulphate does not burn white it
can be fused with one gram of sodium carbonate.   The melt
is then dissolved in water; filtered from $BaCO_3$; the filter
washed with water and the filtrate and washings acidu-
lated with a slight excess of 1 : 1 hydrochloric acid.   Heat
to boiling and precipitate with 10 c.c. of a filtered, satu-
rated solution of barium chloride diluted to 50 c.c. with
water.   Finish as before, *washing this time with water only*.

CHAPTER XII.

MANGANESE IN PIG IRON, TUNGSTEN STEEL, MUCK BAR, NICKEL STEEL, MOLYBDENUM STEEL, VANADIUM STEEL, TITANIUM STEEL AND CHROME STEEL.

First. For pig iron, muck iron, plain carbon or plain vanadium steel, or nickel steel, titanium steel with *absence* of chromium and with silicon not over 1 per cent, and tungsten steel not over 3.5 per cent tungsten, accurate to 2 per cent of manganese. Dissolve 0.100 gram for manganese of not over 1 per cent manganese or 0.050 gram for higher percentages in 40 c.c. 1.20 nitric acid in a 10 by 1 inch test tube over a low Bunsen flame. (See Fig. 5.)

Boil until red fumes are gone. Revolve the tubes from over the flame and add cautiously three grams of light brown colored peroxide of lead free from manganese. Do not use lead peroxide of the very dark brown, in some instances, almost black color, as this very dense variety does not yield its oxygen readily, and results will not check and are frequently 25 per cent too low. Insist on getting light brown lead peroxide.*

After adding the lead to all of the tubes, raise the flames causing the contents to boil, almost to the top of the test tubes, four minutes. Lower the flames, place the tubes *quickly* in cool water, and then, after a few seconds' delay, directly into cold water. Permit the excess of lead perox-

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* Fig. 5 is after a design by Dr. E. S. Johnson.

ide to settle ten minutes, or longer if convenient, in a dark
cupboard.

Decant the contents of the tubes into 5-ounce beakers
as needed, leaving all black sediment in the bottom of the
test tube.   Titrate the pink solution with standard sodium
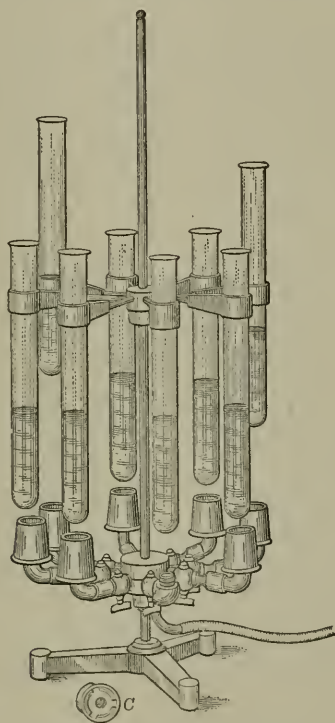
Fig. 5. — Manganese in steel.

arsenite until all pink or brown shades are gone and a
suggestion of yellow color appears. The writer has tried
many methods for the quick determination of manganese,
and can recommend it in preference to other methods
for simplicity, speed and accuracy. Chromium is about

the only disturbing element likely to be met with in steels, and can be quickly removed by the following method, which is used also for all high-speed combinations and high per cent tungsten steels:

Dissolve 0.300 gram or 0.150 gram in low and high manganese steels, respectively, and proceed exactly as given for the determination of manganese in chrome-vanadium steels. (See Analysis of Vanadium Steels.)

For plain molybdenum steels without chromium, proceed as in plain steels. Presence of large quantities of copper and nickel do not interfere with this method. Of course, hydrochloric acid should be absent, or any other substance that would reduce permanganic acid, such as carbonaceous materials. Sunlight bleaches the pink color, causing low results.

Standard Sodium Arsenite Solution.*

Concentrated Stock Solution. 2.48 grams of C.P. arsenious acid and 12.5 grams of C.P. fused sodium carbonate dissolved in 1250 c.c. of distilled water.

Working Strength. 200 c.c. of stock solution diluted with 1600 c.c. of water. One c.c. of this solution will equal, usually, 0.07 per cent of manganese when 0.100 gram of sample is taken. It should be checked against steels of known manganese content before it is used.

* Deshay suggested the sodium arsenite titration.

CHAPTER XII.

SILICON IN PIG IRON, STEEL AND MUCK BAR.

WEIGH 1.5 grams of pig iron into a No. 2 dish. Add
15 c.c. 1 : 3 sulphuric acid plus 10 c.c. water. Weigh 5
grams of low silicon steel or three grams of high silicon
steel, i.e., silicon content of 0.1 per cent and over, into a
No. 5 dish. Add 45 c.c. 1 : 3 sulphuric acid and 25 c.c. of
water. Warm gently until all metal is in solution, adding
more water if necessary, should sulphate of iron form
before effervescence is over. When the iron is in solution
evaporate the pig iron and higher carbon steels directly to
thick fumes of sulphuric anhydride without removing the
covers.

Low carbon steels and chrome steels of 1 per cent chro-
mium and over will bump and spurt from under the covers
if attempt be made to evaporate them rapidly over the
bare flame of the argand burner. In such cases the covers
are rinsed off into the dishes, and the contents of the latter
are evaporated to thick fumes on a graphite or sand bath.

For effecting the solution of the iron and the evapora-
tion to fumes with covers on, an apparatus consisting of a
stand of twelve argand burners covered with a copper-
rimmed asbestos board of twelve holes is used. See Fig. 1,
page 164.

Having evaporated the samples to fumes, the dishes
are cooled and filled conveniently full of distilled water.
They are put on the heating stand; the contents heated
and stirred until all of the sulphate of iron is in solution.

Ashless paper pulp is mixed with the solutions, which are then filtered through 11 cm. ashless filters; the silicious residues washed free from iron test with 1 : 10 hydrochloric acid and then free of acid with water. Potassium sulphocyanate is used in testing for the presence of iron. Wash acid and wash water are applied cold.

The washed residues are ignited in a muffle furnace until pure white. The residues may retain a reddish tint due to iron, or may be colored gray from presence of chromium or copper oxides, or yellow owing to the presence of small quantities of tungsten or vanadium. In such event after having been weighed they should be evaporated to dryness with a few drops of sulphuric acid and 10 c.c. of c.p. hydrofluoric acid. They are then ignited and weighed again, and the silicon content is calculated from the loss of weight, which multiplied by 47.02 and divided by the weight taken yields the percentage of silicon.

When chromium is present, to the extent of 1 per cent, the silica residue can be freed sufficiently from chromium to make a subsequent evaporation with hydrofluoric and sulphuric acids unnecessary by boiling the fumed sulphate residue for ten minutes with a mixture of 75 c.c. of 1 : 1 hydrochloric acid and 75 c.c. of water. Then filter and wash as before.

The ignited residues are cooled in a desiccator, weighed, multiplied by 47.02 and divided by the weight taken.

The silicious residues obtained by this method, or any other of the variations that are in vogue, are liable to be contaminated with titanium and aluminum, especially, in pig iron. Hence all silica residues, for strictest accuracy, should be evaporated with an excess of hydrofluoric acid and two or three drops of sulphuric acid, then ignited and weighed again, multiplying the loss of weight by the usual factor, and dividing by the weight taken to obtain the percentage of silicon.

CHAPTER XIII.

THE ANALYSIS OF GRAPHITE AND GRAPHITE CRUCIBLES.

THE total carbon is determined by direct combustion in the electric furnace. The sample is reduced to sufficient fineness to pass through No. 11 bolting cloth. A hardened steel mortar is used with a ball pestle. The chamber of the mortar is $3\frac{1}{2}$ inches deep by $1\frac{3}{4}$ inches diameter. The total thickness of the steel block is 4 inches, inclusive. The pestle fits, exactly, the bottom of the mortar. The material is pounded into this opening by striking on the end of the pestle with a hammer. It is then taken out and ground in an agate mortar to loosen the mass which is sifted through the bolting cloth. The portion that does not pass the cloth is put back into the steel mortar and hammered again, and so on until the sample all passes through the cloth.

0.200 to 0.300 gram of sample is used, and it burns completely in oxygen in the electric furnace. Forty-five minutes elapse from the time the sample is put in the furnace until the absorption apparatus is detached for the final weighing of the carbon dioxide formed. The weight of the CO_2 multiplied by 27.27 and divided by the weight taken for analysis yields the exact carbon in the sample.

VOLATILE MATTER.

One gram of sample is burned in a platinum crucible with a *slow* stream of oxygen passing in through a hole in the lid of the same. The lid is removed and the contents stirred with a nickel wire at intervals of about twenty min-

utes. The porcelain tube of a Rose crucible is used to con- duct the oxygen through the hole in the platinum lid. When the contents of the crucible no longer lose weight the ignition is stopped. The total loss of weight less the weight of carbon by combustion equals the volatile matter other than carbon, such as water and sulphur.

A direct determination of water can also be made by igniting the substance in a stream of air, dried by passing it through a jar of phosphoric anhydride such as is used in the carbon combustion train. (See Fig. 4 (*J*), page 141.) The sample is put in a clay boat and heated to redness in a porcelain or quartz combustion tube. In the outlet end of the tube is attached, by means of a rubber stopper and glass tube, an absorption jar containing phosphoric acid. The outlet of the absorption jar is guarded against the ingress of moisture by a calcium chloride tube closely filled with bits of stick caustic potash. The air is drawn through by a suction pump. At intervals of twenty minutes the heat is lowered, the passing of the air is stopped and the absorp- tion jar is weighed. It is attached again, the heat raised to redness for another twenty minutes, and the weighing is again made as before, and so on until there is no more gain than is obtained by a blank test carried through in the same manner. The total increase in weight of the phos- phoric anhydride less the blank is calculated to percent- age as water.

A blast lamp flame is used to expel the carbon, obtain the ignition loss, and the ash for analysis. The ash from the one gram taken for ignition loss is analyzed for its various constituents exactly as a clay. It is fused with a mixture of 10 grams of anhydrous carbonate of soda plus one gram of niter in a platinum crucible. The melt is dis- solved out with water in a platinum dish, using heat to hasten the solution. The water extraction is transferred to a No. 6 porcelain dish. The dish is covered with a watch

glass, and 1 : 3 sulphuric acid is allowed to flow down the under side of the lid until 125 c.c. in all have been slowly added. The acidulated fusion is stirred cautiously with a glass rod extending under the cover. The solution is heated until all effervescence is over. The under side of the cover is rinsed off, the washings flowing into the dish. The contents of the latter are then evaporated to thick fumes of sulphuric anhydride. Cool. Add enough water to dissolve the sulphates, heating for about twenty minutes.   Cool again.   Add paper pulp.   Filter and wash with 1 : 10 sulphuric acid.   Wash 60 times, allowing each washing to drain off before the next one is added. The residue on the filter is burned at lowest possible heat until pure white. The heat is then raised to blast for ten minutes. The crucible is cooled in a desiccator and weighed. The contents are blasted again, or until no further loss occurs. A few drops of sulphuric acid are added, the crucible is filled to about two-thirds its capacity with hydrofluoric acid and evaporation in a good draft to fumes of sulphuric acid follows. The sulphuric acid is driven off, the crucible is heated to bright red and weighed again. The loss of weight is the silica, which multiplied by 100, and divided by the weight taken, yields the percentage of the latter oxide.

The filtrate from the silica is reduced with 10 grams of zinc and titrated for iron with potassium permanganate to first pink that lasts for a few seconds. The iron is calculated to oxide.

If alumina is also wanted, the filtrate from the silica is first precipitated in a No. 7 porcelain dish in about a 600 c.c. volume with the faintest possible excess of ammonia water which has been filtered free of any sediment or scales of glass. When the solution is faintly ammoniacal it is boiled, cooled, and ashless paper pulp added in sufficient quantity to secure rapid filtration and washing. The aluminum and

iron hydroxides are washed free from sulphates with ammonium nitrate water. The washings are tested with barium chloride, and when no milkiness forms in the former on addition of the chloride, the precipitate is given ten more washings. The filter and precipitate are burned cautiously in a weighed platinum crucible after first drying out some of the excessive amount of water held by the pulp. The paper pulp is roasted out and the ash ignited to a constant weight with a blast lamp. The precipitate is calculated as alumina, plus oxide of iron. All of the phosphorus present in the graphite will be counted as alumina unless it is desired to separate it. In that event the solution should be divided before the ammonia precipitation is made. Pour it into a 500 c.c. flask. Dilute to the 500 c.c. mark with water. Mix the contents thoroughly and pour enough of the latter into a 250 c.c. flask to fill it to the mark.

This gives two portions; one is reduced at once with zinc and titrated with permanganate for iron. The permanganate standard is made by dissolving 0.727 gram of potassium permanganate in water and diluting it to 1000 c.c. 1 c.c. of this standard equals 0.001284 gram of iron. In a burned pot the iron is calculated to ferric oxide. Therefore the iron found in parts of a gram is multiplied by 10 and divided by 7 to obtain the amount of ferric oxide. It is necessary to make this calculation in all cases where alumina is asked for. In a plumbago, or graphite, it is usually customary to calculate the iron to protoxide (Fe O). To obtain the amount of the latter, multiply the weight of metallic iron found by $\frac{9}{7}$. These weights of oxide are then reduced to percentage in the usual way.

PHOSPHORUS AND ALUMINA.

The other 250 c.c. portion of the divided sulphate fil-
trate is precipitated with a faint excess of ammonia, washed,
roasted, blasted to constant weight as Al_2O_3, Fe_2O_3, P_2O_5.
The ferric oxide found in the 250 c.c. reduced with zinc,
is deducted from the total weight of the three oxides found
in the second portion. This leaves Al_2O_3, P_2O_5. The
phosphorus is obtained by fusing the oxides with twenty
times their total weight of sodium carbonate, plus four
times their weight of potassium nitrate. The melt is
dissolved in a few c.c. of water, filtered into a 5-ounce
beaker, washing the filter thoroughly with ammonium
nitrate water. The filtrate is acidulated with 1.20 nitric
acid, boiled with a slight excess of permanganate solution
(see Phosphorus in Steel), and the phosphorus is finished
as in steel. The phosphorus obtained is calculated to the
pentoxide (P_2O_5) as follows: For example, suppose 10 c.c.
of the alkali standard were used, then $10 \times 0.0001 \times 1.63$
equals 0.00163, which multiplied by $\frac{71}{31}$ equals the phos-
phorus pentoxide to be deducted from the weight of
Al_2O_3, P_2O_5. This leaves the alumina which came from the
0.500 gram of sample. It is reduced to percentage by the
usual calculation. If phosphorus is not asked for, it is
unnecessary to divide the sulphate filtrate from the silica.
It can be precipitated with ammonia, filtered, washed,
roasted, ignited, and weighed as Al_2O_3, Fe_2O_3, ignoring the
presence of phosphorus, which is not likely to introduce
a serious error. The total oxides are then fused with 10
grams of sodium carbonate, the melt dissolved in excess
of 1 : 3 sulphuric acid (about 85 c.c. of the acid); reduced
with zinc and titrated with permanganate. The iron is
calculated to Fe_2O_3 and deducted from the Al_2O_3 and
Fe_2O_3 to obtain alumina.

LIME AND MAGNESIA.

If lime and magnesia are asked for, the ash from the graphite is fused as before, but is acidulated with an excess of hydrochloric acid instead of sulphuric acid.

The silica is removed by evaporating twice to hard dryness and filtering between evaporations. It is washed with 1 : 10 hydrochloric acid. The filtrate and washings are precipitated with a slight excess of ammonia that has been freed from carbon dioxide as follows: The ammonia water is put in a sulphur flask fitted with a No. 6 stopper through which passes a glass tube. This tube is connected by rubber tubing with a jar such as shown in Fig. 3, page 140, filled with short pieces of stick caustic potash. The connection is with the top of the jar. The ammonia water in the flask is heated by a Bunsen burner. This drives the concentrated ammonia from the flask over into the jar of caustic potash, which removes the CO_2. The purified ammonia passes out at the bottom, and from thence via more rubber tubing it reaches the glass delivery tube, which dips into a reagent bottle containing distilled water that has been boiled for half an hour and cooled without stirring. The ammonia is passed into this bottle until the water in it smells strongly of ammonia. The carbon dioxide-free ammonia is used for all separations of iron from lime.

The filtrate from the iron and alumina is concentrated to 300 c.c. and made faintly ammoniacal. If the presence of manganese is suspected, a slight excess of bromine is added, and the solution is heated until the brown flakes of manganese separate. This is not done unless the carbonate and nitrate fusion of the original ash is noticeably green.

The hot faintly alkaline filtrate is treated with 20 c.c. of saturated solution of ammonium oxalate to precipitate the calcium as oxalate. The latter is permitted to settle several hours. It is then filtered out and washed with hot

water containing a little ammonium oxalate, until free of chlorine test with silver nitrate solution.* The precipitate is roasted until white and blasted to constant weight. It is weighed as calcium oxide, which is calculated, as such, to percentage. The filtrate from the lime is acidulated with HCl, concentrated to a small volume; filtered; made slightly ammoniacal; cooled; 10 c.c. of saturated solution of microcosmic salt are added, and then the total volume is increased one-fourth with concentrated ammonia. After thorough stirring, the precipitate of ammonium magnesium phosphate is permitted to settle until the next day. It is filtered on a small filter and washed forty times with a mixture of one part of water and three parts of concentrated ammonia. It is then burned at a low red-heat until white, and weighed as magnesium pyro-phosphate, which contains 36.24 per cent magnesium oxide.

The filtrate and washings should be treated with more phosphate solution, and, if an appreciable precipitate forms, it is collected, washed, ignited, weighed, and added to the principal residue.

SILICON CARBIDE.

When complete analyses of old pots that present a green-colored fracture are made, the analytical data will give evidence of the presence of silicon existing in the reduced state, that is not entirely as oxide. If the silica, alumina, iron oxide and lime obtained are calculated as such and to this is added the total carbon as found by the RED LEAD process, the percentages may reach the impossible total of 115.8 per cent in some instances. Such pots when broken present a greenish fracture. When the writer first encountered this difficulty he was somewhat puzzled. Such material cannot be burned free of black

* Acidulate the washings with a few drops of 1.20 nitric acid before testing for chlorine.

or gray residue in a stream of oxygen. This is characteristic of silicon carbide. The combination will not yield its carbon in the electric furnace with oxygen alone. It decarbonizes readily if burned with red lead. For carbon 0.300 gram of green fracture pots is burned with 4 grams of red lead. The blank due to the red lead is deducted, and the carbon percentage calculated as in pots free from silicon carbide. The ignition loss, which, in a burned pot, will ordinarily check within 0.1 to 0.2 per cent of the red lead result, will fall below the total carbon as much as six or seven per cent in the old pots containing the silicon carbide, due to the fact that the carbon cannot be burned out of the silicon carbide except with red lead.

The writer estimated the carbide as follows: The total carbon obtained by red lead combustion and the ignition loss obtained by blasting in a stream of oxygen were both calculated to a one gram basis. The weight of carbon by ignition loss was deducted from the weight of the total carbon. The remainder was calculated to silicon carbide. Then the excess of per cents above 100 per cent was assumed to be oxygen. The amount of silicon required to combine with this oxygen was calculated. The silicon was then figured to carbide. The per cent of carbide gotten in this manner checked fairly well with that found by calculating from the difference between the total carbon and the ignition loss. The silicon required to combine with the silicon carbide found was calculated to silica and deducted from the total silica. The carbon remaining after the ignition in oxygen was deducted from the total carbon. A sample analysis of an actual case is appended.

	Per cent
Free carbon....	38.92
Silicon carbide	20.14
Iron oxide (FeO)	4.37
Alumina	15.11
Free silica	20.47
Lime	.98
	99.99

Calculations for Silicon Carbide

After having made a number of determinations of silicon carbide in old pots, with green fracture, the author has found it more satisfactory to obtain the total percentage footing of the oxides and carbon. Assuming the excess above 100 per cent to be due to silicon existing as carbide, instead of oxide, the calculations are as follows:

ANALYTICAL DATA (EXAMPLE).

Total carbon............................	44.90
Total " silica " obtained	50.60
Alumina................................	15.11
Total iron calculated as protoxide (FeO)..	4.37
Lime...................................	.98
Total...............................	115.96

Free Silica. This gives on a one gram basis 159.6 milligrams excess, which is assumed to be oxygen. This is equivalent to 30.12 centigrams of silica:

$$Si + O_2 = SiO_2$$
$$O_2 : SiO_2 \quad :: \quad O_2 \quad : \quad SiO_2$$
$$32 : 60.4 \quad :: \quad 159.6 \quad : \quad x$$
$$x = 30.124 \text{ centigrams } SiO_2,$$

to be deducted from the total silica, or 50.6 minus 30.124 equals 20.47, or 20.47 per cent free silica in the pot.

Silicon Carbide. Silica is reduced to silicon by the factor .4702, therefore the 30.124 centigrams of silica correspond to 30.124 × .4702 equals 14.16, or 14.16 per cent silicon. This is equivalent to 20.14 centigrams of silicon carbide.

$$Si + C = SiC$$
$$Si : SiC \quad :: \quad Si : SiC$$
$$28.4 : 40.4 :: 14.16 : \quad x$$
$$x \text{ equals } 20.14 \text{ or } 20.14 \text{ SiC in the pot.}$$

Free Carbon. The 20.14 centigrams of silicon carbide correspond to 5.98 centigrams of carbon to be deducted from the total carbon found:

$$C + Si = SiC$$
$$C : SiC :: C : SiC$$
$$12 : 40.4 :: x : 20.14.$$

x equals 5.98, or 44.90 minus 5.98 equals 38.92, or per cent of free carbon in the pot.

RESULTS.

Excess of Oxygen Calculated to Silicon Carbide.	Excess of Oxygen Calculated to Silicon.	
38.92% carbon (free)	44.90%	total carbon
20.14% silicon carbide	14.16	silicon
4.37% protoxide of iron	4.37	iron oxide
15.11% alumina	15.11	alumina
0.98% lime	.98	lime
20.47% silica	20.47	silica
99.99	99.99	

SULPHUR IN POTS AND GRAPHITES.

Fuse one gram of sample with a mixture of 10 grams of sodium carbonate ground intimately with 10 grams of potassium nitrate. Such a mixture must be heated cautiously as it will flash if heated too quickly. When the first action is over, heat until the fusion is completely molten and keep it so with the least possible heat for a half hour. Cool; dissolve the melt with water; acidulate with hydrochloric acid in a 600 c.c. casserole. Heat with cover on until all effervescence is over, rinsing same; evaporate to dryness and finish as sulphur in ferrovanadium of high silicon content. If such a fusion is heated too hot it will boil out of the crucible.

.

Standardization of Permanganate for Iron.

Weigh into a small flask 0.062 gram of oxalic acid c.p.   Put into this flask 50 c.c. distilled water and 20 c.c. 1:3 sulphuric acid.   Warm the solution until the crystals are dissolved and titrate it hot.   Do not let the solution boil. It will usually require 43.1 c.c. of this permanganate to change the oxalic acid solution to a slight pink.   Deduct 0.2 c.c. blank.   Therefore 0.062 divided by 42.9 $\times$ 8 divided by 9 equals 0.001284 or one c.c. of the permanganate solution equals 0.001284 gram of iron.   The value of any permanganate solution in terms of oxalic is multiplied by $\frac{8}{9}$ to obtain its iron value.

For a check, weigh 0.065 gram of oxalic acid.   This will require 45.2 c.c. to render it pink.   Therefore 0.065 divided by 45.0 $\times$ 8 divided by 9 equals 0.001283, or 1 c.c. standard solution equals 0.001283 gram of iron.

0.727 gram of $KMnO_4$ is dissolved in 1 liter of water for the above standard.

CHAPTER XIV.

THE ANNEALING OF STEEL.

AFTER several years of experience with the annealing of steel, during which careful records were kept with a Le Chatelier pyrometer, the writer came to certain conclusions as to the proper temperatures for annealing plain carbon steels and alloy steels.

The pyrometer was sent to the bureau of standards for the verification of its readings.

Briefly the results are as follows:

ANNEALING TEMPERATURES.

First. Cast steel of all kinds that has *never been reheated* should be first brought to a temperature of 850° C., and held there for one hour. The heat should then be lowered as quickly as possible to 700 to 720° C. and held at that temperature for ten to twelve hours. The pipes can then be drawn and the steel can be cooled as quickly as desired. The fact is, that if the steel is once perfectly annealed, it can be withdrawn from the furnace, thrown into water and it will be as soft as ever. The author took two pieces of steel from the same saw plate and annealed them, one lying on top of the other, until he knew both were perfectly annealed. He then withdrew the pieces from the furnace. One was thrown directly from the annealing furnace into a bucket of cold water while still at the *annealing* heat. The companion piece was cooled in the air. Both pieces were then pulled in the testing machine

and registered identically as to tensile strength and elongation, etc. Steel once perfectly annealed can only have its softness impaired by heating above the annealing range. Rapid cooling of *perfectly* annealed steel has no effect whatever on its softness.

However, if the annealer has lowered the heat before the steel has been entirely annealed, or in other words has not held it long enough within the range of temperature where that particular steel anneals most quickly, he stands a better chance of getting his steel eventually soft enough for the purpose intended by burying it in ashes or lime. He thus, in reality, holds it longer within the range of temperature where steel anneals *slowly*. That is, the steel passes more slowly through the range of *slow* annealing, being the temperatures below 720° C., than if it had *not* been surrounded by more or less non-heat-conducting substances.

Second. The author has found, that plain carbon steels, no matter whether the carbon be 0.50 per cent or 1.40 per cent, anneal best and most quickly between 700 and 720° C.

This is also true of most chrome-tungsten and chrome-molybdenum steels. It is particularly noticeable in high speed steels, for if one wishes to drill a high speed test he can render it soft enough by annealing it for one hour at 720 degrees, whereas it will require two to three times that length of time to accomplish the same softening at lower ranges.

Third. On the other hand, high manganese and high nickel content lower the annealing heat. Seven per cent nickel steel anneals to the perfectly annealed state of the carbon at 520 to 550° C. Again, Hadfeld's manganese steel the writer has succeeded in softening so that it could be drilled without dulling a high speed tool at a temperature of 520 to 550 degrees. The specimen

of this steel that the writer first experimented with was of
the following analysis:

	Per cent
Carbon	1.40
Manganese	13.42
Silicon	.043
Phosphorus	.047
Sulphur	.030

Plates of the steel, before annealing, could not be drilled
even with a high speed drill. After 24 hours annealing a
plate was drilled without sharpening the bit and the
latter drilled the plate without "screeching." In fact,
four holes were made in such a plate without resharp-
ening. These plates were then taken to the planer and
machined easily, but they presented the peculiar prop-
erty of being very brittle. The condition of the carbon by
the acid annealing test showed that the carbon had
attained almost entirely to the perfectly annealed state.

Fourth. Steel that has been reheated and rolled or
hammered need not be heated above 720° C. However, if
the furnace is heated to 800 degrees, for example, and a lot
of steel is charged into it, it can be brought to 720 degrees
more quickly. The large body of cold steel will absorb its
surplus heat.

Overheated Steel. If steel ingots are allowed to lie
in soaking pits or reheating furnaces at temperatures
approximating welding heats for considerable time, the
annealer's task will be greatly complicated, as such steel is
much harder to bring into the annealed state.* Bad
cases of overheating or prolonged soaking at high heats
will require two or three times as long to anneal at the
regular temperature. There seems to be nothing to do
in such cases but to re-anneal until the carbon is finally
brought again into the perfectly annealed condition.

Fifth. It is indeed remarkable that plain carbon cast

* By reason of the very coarsely crystalline structure formed by
the excessive heat.

steel as it comes from the mold can be refined from the most coarse crystalline structure ever found in the raw cast steel to a fine silky fracture by *heat alone*, before it is hammered, rolled or forged in any manner. To accomplish this great change it is merely necessary to heat the steel first as it comes from the mold to 850° C. for one hour, and then lower the heat to 720° C. and hold the steel at this temperature for twelve to fifteen hours. Then lay it out to cool wherever convenient. A complete anneal, as already stated, is secured in this manner.

Sixth. Steel that has been heated to 800 to 850° C. and quenched quickly in water or oil will attain the perfectly annealed condition within thirty minutes to one hour's time at a temperature between 660 and 690° C., whether the carbon be 0.50 or 0.90 per cent.

FORMATION OF GRAPHITIC CARBON AND BLACK FRACTURE.

On three different occasions the writer was called upon to investigate the temperature most favorable to the formation of graphitic carbon, or in other words, to ascertain the real cause of its presence. As a result of extended experimental annealing of cold rolled steel the author has come to assign the cause largely to annealing, only, within a range of temperature that causes the carbon to assume the uncombined state.

As mentioned, on three different occasions, three different lots of cold rolled steel, coming from different steel works, were subjected to prolonged annealings, and the progress of the formation of the graphitic carbon was noted.

In two lots the cold rolled steel was free from even traces of the graphite at the beginning of the anneals. Anneals were continued in some instances for 100 hours, but most periods did not aggregate over 40 hours.

Anneals were interrupted at 8 to 12-hour intervals to make annealing and graphite tests. Further, a 1.30 carbon tool steel *ingot* was put in a lathe and turned down until there was nothing left of it but a ⅜-inch rod. By prolonged annealing between the range of 660 to 700 degrees black fracture was produced. This was raw cast steel that had never been hammered or rolled or forged in any way. The conclusions are as follows:

First. The higher percentages of carbon yield the black fracture most quickly, the range from 1.20 per cent carbon and above being the most favorable. Percentages under 1.00 per cent carbon are perhaps free from appreciable amounts of graphitic carbon, at least under any conditions likely to be met with in practice.

Second. The temperature most favorable to the quick formation of graphite lies between 660 and 700° C.

Third. The least favorable temperature for its formation, within the annealing and *cold rolling* range, is below 600 degrees. The other extreme of temperature, 720° C., is also less favorable to its formation, but scaling goes on so fast as to give undesirable finish.

Fourth. The reason that black fracture is associated with cold rolling is that during this process the steel is worked and repeatedly reheated within the range of temperature where graphite forms rapidly. The steel has really had a series of anneals between 660 and 700° C.

Fifth. The longer the anneal is continued *at any annealing* temperature, the more graphite will be formed.

Prior to cold rolling, that is, when the steel gets its very first anneal for softening purposes only, hold it at 700 to 720° C. Keep it as near the highest annealing heat as possible, as by so doing a quick anneal is obtained without formation of graphite.

But when reheatings occur during cold rolling do this reheating at the lowest heat practicable, for around

580–600° C. graphite does not form as fast as at 660–700 degrees, nor does scale. *Let the periods of annealing and reheating be as short as possible.*

Sixth. By heating steel to 950–1000° C. for one or two hours, then turning down the gas so that the steel cools in the furnace to 660–700 degrees, and continuing to anneal at the latter temperature for a given length of time, graphite can be eventually formed in steel with carbon as low as 1.04 per cent. Therefore steel that is to be cold rolled should not be allowed to remain long in soaking pits or heating furnaces at high temperatures.

Steel containing chromium is not likely to contain graphite even with carbon as high as 1.27 per cent and chromium as low as 0.6 per cent. The writer succeeded in starting a graphitic formation in such a steel only by heating it to 900–1000° C., for an hour or two before annealing at 660–700° C. In neither this instance nor in the case of the 1.04 carbon plain steel did there seem to be any appreciable tendency for a gradual growth of the graphite due to prolonged annealing only, even after the eleventh trial, making considerably over 100 hours anneal. Perhaps if these samples had been again heated to 1000 degrees before each of the eleven anneals, an appreciable growth of graphite would have been noted. In neither instance was there enough graphite formed to be noticeable in the fracture.

To detect small amounts of graphite dissolve 0.100 gram of sample in a 152.4 mm. × 16 mm. tube (6 inches × 16 mm.) with 4 c.c. 1.20 nitric acid and heat on a water bath in boiling water for two hours in the case of chrome steel and one hour in plain carbon steel. Permit the solution to stand for several hours without agitation of the same to detect traces of graphite which can be plainly seen in this way in the bottom of the tube.

Acid Test for Annealing.

Dissolve 0.100 gram of sample in 4 c.c. of cold 1.20 nitric acid. Examine immediately in daylight. If the undissolved carbon is flaky and floats about in the solution the steel is not annealed at all. It is in the condition in which it left the rolls or hammers. If on the other hand the carbon is in an extremely fine state of division, so much so that it does not separate in flakes at all, but rather tends to run up the sides of the test tube in a thin film, then the annealing is perfect and the steel has reached the highest degree of softness.

In perfectly annealed steel this finely divided annealed carbon will remain in almost complete suspension for some minutes. Indeed it cannot be seen to collect and settle as flakes, but settles imperceptibly, after some time, so that there exists a collection of fine powder, rather than flakes, in the bottom of the test tube. An ordinary 6 inch × 15 mm. carbon test tube is best suited for these tests. Then, if it is desired to examine the sample for graphitic carbon, the tube is put at once on a water bath in boiling water for one hour. By that time all of the combined carbon will have gone into solution and the graphite will be collected in a coal-black residue in the bottom of the tube.

The operator soon learns to pronounce to an absolute certainty whether the steel is *perfectly* annealed or not. He also can judge whether much or little graphitic carbon is present.

This annealing test is carried out in ten minutes, and enables the chemist to pronounce unfailingly on the quality of the annealing before the steel is shipped to the customer. It gives a perfect control over the work that is being done by the man in charge of the annealing. A scale of annealing can be established. It has been the

writer's custom to call perfect annealing, 5 degrees. Good enough for all practical purposes, $4\frac{1}{2}$ degrees. Moderately good, 4 degrees. Partially annealed, 3 degrees and so on. The quicker the carbon forms in flakes and separates, the poorer the annealing. As stated, good annealed carbon does not separate in flakes at all.

Annealing Test When Alloys Are Present.

When from 0.1 per cent to 1 per cent chromium is present in steel the annealing *carbide* is formed and acts differently from carbon in plain steel. It forms almost coal black; is not flaky, but the individual grains are coarser than in plain carbon steel.

A well annealed chrome carbide within the above chromium content forms in minute coal-black grains that settle rapidly to the bottom of the test tube. The quicker the grains form, the blacker they are, and the more rapidly they settle to the bottom, the better the anneal.

This peculiarity constitutes an infallible test for the presence of chromium in steel, but the latter must be perfectly annealed to show as small a quantity as 0.1 per cent chromium in 0.100 gram of sample. More experience is required to pronounce on the annealing of chrome steel by the acid test, but with practice one can be quite as accurate as when making the test on plain carbon steel.

Nickel and manganese steels act exactly as plain carbon steel when perfectly annealed. The color of the finely divided annealed carbon has perhaps more of a

In well annealed steel containing 3% of chromium and over, the carbide is coal black but does not settle to the bottom nearly so fast as does the carbide found in perfectly annealed steel of one per cent chromium and under. The grains settle slowly, and there is a well defined film running up the walls of the test tube.

Plain tungsten steel, in the perfectly annealed state, gives practically the same appearance as ordinary carbon steel when tested for annealing.

brown shade in high manganese and nickel steels, but it does not settle any faster than in plain carbon steels. One of the greatest difficulties in annealing steel is to obtain uniform heat throughout the entire furnace. The dividing line between a good annealing heat and hardening temperature is very sharp. The writer has had a piece of steel but two inches long exhibit perfect annealing on one end, while the other end had passed into the hardening range. He has also another piece that shows black fracture on one end, and the other end less than two inches away shows no trace of black fracture. These phenomena are due to unequal temperature in the furnace.

An annealing furnace should have several pyrometer couples located in different parts of it.

The pyrometers should be sent to the Bureau of Standards for occasional verification of their readings. They should not be used until their accuracy has been verified, as different instruments are liable to disagree as much as 25° C. from the Washington Standard.

CHAPTER XV.

THE PERCENTAGE REDUCTION OF A SUBSTANCE IN SOLUTION TO ANY DESIRED PERCENTAGE.

LET P = the percentage of the substance in the concentrated solution.

Let p = the lower and desired percentage of the substance.

Let A = the specific gravity of the concentrated solution.

Let W = the amount of water necessary to add to 1 c.c. of the conc. solution to reduce it to the desired lower percentage.

Then
$$W = \left(\frac{P - p}{p} \right) A.$$

CALCULATIONS.

Suppose the specific gravity of a given sample of nitric acid is found by means of a hydrometer to be 1.400 at a temperature of 20° C. By table No. 1 we find that the difference in specific gravity for 1° C. between 1.37 sp. gr. and 1.405 is 0.0013 to 0.0014, or a total difference of 0.0001 for a variation of 0.035 in specific gravity. Now 1.400 is 0.030 above 1.37 in specific gravity, therefore the correction for 1 degree at 1.400 is 0.0013 plus $\frac{30}{35}$ of 0.0001, or 0.0013 plus 0.000085, or 0.001385. Since the temperature was 20 degrees, then the specific gravity of the given acid if cooled to 15 degrees would be 1.40 plus 0.00138 × 5, or 1.4069. By the table we find that the nearest specific gravity, or 1.405, gives a percentage of 66.40. Further, the percentage correction at this point for 0.001 of

specific gravity is 0.220. Therefore, the percentage of the given concentrated acid at 15 degrees would be 66.40 plus 0.220×1.9, or 66.4 plus 0.418, or 66.818, or P in the reduction formula.

For example, if it is desired to reduce this 66.818 per cent acid at 15 degrees to 32 per cent acid at 15 degrees, then we have $\dfrac{66.818 - 32.00}{32.00} \times 1.4069$, or $\dfrac{34.818}{32} \times 1.4069$, or 1.088×1.4069, or 1.530, or every cubic centimeter of the acid requires 1.5307 c.c. of water to reduce it to 32 per cent at 15° C. By consulting table No. 2 it will be seen that 1000 c.c. acid of 1.407 specific gravity requires 1531.8 c.c. of water to reduce it to 32 per cent acid at 15° C.

In like manner, if it is required to obtain 20 per cent acid from 66.818 per cent acid: $\dfrac{66.818 - 20}{20} \times 1.4069$, or $\dfrac{46.818}{20} \times 1.4069$, or 2.3409×1.4069, or 3.2934. That is, 1 c.c. of 66.818 per cent acid requires 3.2934 c.c. of water to dilute it to 20 per cent acid at 15° C.

Use of Table No. 2.

Having by means of table No. 1 calculated the observed specific gravity to 15 degrees, then from table No. 2 the amount of water required to reduce such 'an acid to 32 per cent or 20 per cent is read either direct or by interpolation.

In a similar way one can reduce concentrated ammonia to any desired lower percentage, the only difference being that in calculating to 15° C. the correction for percentage is subtractive instead of additive as in the case of acids. The reason, of course, being that the greater the density of ammonia solution in water, the lower the percentage of NH_3 therein.

If one needs to prepare from concentrated ammonia an 11.50 per cent solution, first, dilute two parts of the former with one part of water and cool to the room temperature. Let the reading be 0.9385 at 23° C. The correction for 1° C. at 0.938 by table No. 3 is 0.0004 for sp. gr. The total correction for the 8 degrees is 0.0004 × 8, or 0.0032. This makes the specific gravity of the ammonia at 15 degrees to be 0.9385 plus 0.0032, or 0.9417. By the table the nearest lower sp. gr. is 0.940, which corresponds to 15.63 per cent ammonia. The percentage correction for 0.001 of sp. gr. at this point is 0.295. Therefore the total correction is 0.295 × 1.7, or 0.5015. Hence, the percentage for a specific gravity of 0.9417 is 15.63 − 0.5015, or 15.1285. To reduce this percentage to 11.50 the formula gives the following:

$$\frac{15.128 - 11.50}{11.50} \times 0.9417$$ equals 0.297, or 1 liter of this

ammonia would require 297 c.c. of water to dilute it to 11.50 per cent at 15° C.

For further illustration, suppose it is necessary to obtain the percentage of ammonia corresponding to a specific gravity of 0.947 at 22 degrees. The correction for specific gravity per one degree of temperature at the nearest point in the table (0.946) is 0.00036. As the reading was taken 7 degrees above the 15 degrees, then the total correction is 0.00036 × 7, or 0.00252, and the corrected reading is 0.947 plus 0.00252, or 0.9495. The nearest lower specific gravity in table No. 3 is 0.948, being equivalent to a percentage of 13.31. Now the correction for percentage at this point is 0.285 for every 0.001 of specific gravity. The total correction is 0.285 × 1.5, or 0.427. The percentage of the ammonia for 0.9495 at 15 degrees is 13.31 − 0.427, or 12.88 per cent.

AQUEOUS SOLUTIONS OF NITRIC ACID.

From a Table by Lunge and Rey.

Specific Gravities and Percentages HNO$_3$.

Specific Gravity $15°$ $d \frac{15°}{4°}$ C.	Percentage. HNO$_3$.	Difference in Specific Gravity for 1° C. between 13° and 17°.	Difference in Percentage for 0.001 Specific Gravity.	Specific Gravity $15°$ $d \frac{15°}{4°}$ C.	Percentage. HNO$_3$.	Difference in Specific Gravity for 1° C. between 13° and 17°.	Difference in Percentage for 0.001 Specific Gravity.
1.055	9.84	0.0003		1.280	44.41	0.0009	0.154
1.060	10.68	0.0003	0.168	1.285	45.18	0.0010	0.154
1.065	11.51	0.0003	0.166	1.290	45.95	0.0010	0.154
1.070	12.33	0.0003	0.164	1.295	46.72	0.0010	0.154
1.075	13.15	0.0004	0.164	1.300	47.49	0.0010	0.154
1.080	13.95	0.0004	0.160	1.305	48.26	0.0010	0.154
1.085	14.74	0.0004	0.158	1.310	49.07	0.0010	0.162
1.090	15.53	0.0004	0.158	1.315	49.89	0.0011	0.164
1.095	16.32	0.0004	0.158	1.320	50.71	0.0011	0.164
1.100	17.11	0.0004	0.158	1.325	51.53	0.0011	0.164
1.105	17.89	0.0005	0.156	1.330	52.37	0.0011	0.168
1.110	18.67	0.0005	0.156	1.335	53.22	0.0011	0.170
1.115	19.45	0.0005	0.156	1.340	54.07	0.0011	0.170
1.120	20.23	0.0005	0.156	1.345	54.93	0.0011	0.172
1.125	21.00	0.0005	0.154	1.350	55.79	0.0011	0.172
1.130	21.77	0.0005	0.154	1.355	56.66	0.0012	0.174
1.135	22.54	0.0006	0.154	1.360	57.57	0.0012	0.182
1.140	23.31	0.0006	0.154	1.365	58.48	0.0012	0.182
1.145	24.08	0.0006	0.154	1.370	59.39	0.0013	0.182
1.150	24.84	0.0006	0.152	1.375	60.30	0.0013	0.182
1.155	25.60	0.0006	0.152	1.380	61.27	0.0013	0.194
1.160	26.36	0.0006	0.152	1.385	62.24	0.0013	0.194
1.165	27.12	0.0007	0.152	1.390	63.23	0.0013	0.198
1.170	27.88	0.0007	0.152	1.395	64.25	0.0013	0.204
1.175	28.63	0.0007	0.150	1.400	65.30	0.0013	0.210
1.180	29.38	0.0007	0.150	1.405	66.40	0.0014	0.220
1.185	30.13	0.0007	0.150	1.410	67.50	0.0014	0.220
1.190	30.88	0.0007	0.150	1.415	68.63	0.0014	0.226
1.195	31.62	0.0007	0.150	1.420	69.80	0.0014	0.234
1.200	32.36	0.0007	0.148	1.425	70.98	0.0014	0.236
1.205	33.09	0.0008	0.146	1.430	72.17	0.0014	0.238
1.210	33.82	0.0008	0.146	1.435	73.39	0.0014	0.244
1.215	34.55	0.0008	0.146	1.440	74.68	0.0015	0.258
1.220	35.28	0.0008	0.146	1.445	75.98	0.0015	0.260
1.225	36.03	0.0008	0.150	1.450	77.28	0.0015	0.260
1.230	36.78	0.0008	0.150	1.455	78.60	0.0015	0.264
1.235	37.53	0.0008	0.150	1.460	79.98	0.0015	0.276
1.240	38.29	0.0008	0.152	1.465	81.42	0.0015	0.288
1.245	39.05	0.0008	0.152	1.470	82.90	0.0015	0.296
1.250	39.82	0.0009	0.154	1.475	84.45	0.0015	0.310
1.255	40.58	0.0009	0.152	1.480	86.05	0.0015	0.320
1.260	41.34	0.0009	0.152	1.485	87.70	0.0015	0.330
1.265	42.10	0.0009	0.152	1.490	89.60	0.0015	0.420
1.270	42.87	0.0009	0.154	1.495	91.60	0.0016	0.400
1.275	43.64	0.0009	0.154	1.500	94.09	0.0016	0.498

TABLE NO. 2.

DILUTION OF CONCENTRATED NITRIC ACID

To 20 and 32 Per Cent.

Specific Gravity HNO$_3$ at 15°C.	Water Added to 1000 c.c.		Varia-tion in Weight, Water, for 1°C.	Specific Gravity HNO$_3$ at 15°C.	Water Added to 1000 c.c.		Varia-tion in Weight, Water, for 1°C.
	20 Per cent.	32 Per cent.			20 Per cent.	32 Per cent.	
1.395	3086.4	1405.9	1.38	1.433	3790.5	1831.7	1.88
1.396	3103.3	1415.8	1.39	1.434	3810.6	1843.9	1.90
1.397	3120.2	1425.7	1.40	1.435	3830.7	1856.1	1.91
1.398	3137.1	1435.7	1.41	1.436	3852.0	1869.0	1.92
1.399	3154.0	1445.6	1.42	1.437	3873.3	1881.9	1.94
1.400	3171.0	1456.9	1.43	1.438	3894.6	1894.8	1.96
1.401	3188.7	1467.1	1.44	1.439	3915.9	1907.7	1.98
1.402	3206.4	1477.4	1.46	1.440	3937.0	1920.6	2.00
1.403	3224.1	1487.6	1.47	1.441	3958.5	1933.7	2.02
1.404	3241.8	1497.9	1.48	1.442	3980.0	1946.8	2.03
1.405	3259.6	1510.4	1.49	1.443	4001.5	1959.9	2.05
1.406	3277.8	1521.1	1.50	1.444	4023.0	1973.0	2.06
1.407	3295.5	1531.8	1.52	1.445	4044.6	1986.0	2.07
1.408	3313.2	1542.5	1.53	1.446	4066.2	1999.2	2.09
1.409	3330.9	1553.2	1.55	1.447	4087.8	2012.4	2.10
1.410	3348.8	1564.2	1.57	1.448	4109.4	2025.6	2.11
1.411	3367.2	1575.3	1.58	1.449	4131.0	2038.8	2.12
1.412	3385.6	1586.4	1.59	1.450	4152.8	2051.8	2.13
1.413	3404.0	1597.5	1.60	1.451	4175.1	2065.2	2.15
1.414	3422.4	1608.6	1.61	1.452	4197.4	2078.6	2.17
1.415	3440.6	1619.7	1.62	1.453	4219.7	2092.0	2.19
1.416	3459.6	1631.2	1.63	1.454	4242.0	2105.4	2.21
1.417	3478.6	1642.7	1.65	1.455	4263.2	2118.8	2.22
1.418	3497.6	1654.2	1.66	1.456	4286.3	2132.9	2.24
1.419	3516.6	1665.7	1.68	1.457	4309.4	2147.0	2.25
1.420	3535.8	1677.4	1.70	1.458	4332.5	2161.1	2.26
1.421	3555.1	1689.1	1.70	1.459	4355.6	2175.2	2.27
1.422	3574.4	1700.8	1.70	1.460	4378.5	2189.1	2.28
1.423	3593.7	1712.5	1.70	1.461	4402.6	2203.7	2.30
1.424	3613.0	1724.2	1.70	1.462	4426.7	2218.3	2.32
1.425	3632.3	1735.8	1.72	1.463	4450.8	2232.9	2.34
1.426	3651.9	1747.6	1.72	1.464	4474.9	2247.5	2.36
1.427	3671.5	1759.4	1.74	1.465	4499.0	2262.3	2.38
1.428	3691.1	1771.2	1.77	1.466	4523.8	2277.5	2.41
1.429	3710.7	1783.0	1.79	1.467	4548.6	2292.7	2.44
1.430	3730.2	1795.1	1.82	1.468	4573.4	2307.9	2.47
1.431	3750.3	1807.3	1.84	1.469	4598.2	2323.1	2.50
1.432	3770.4	1819.5	1.86	1.470	4623.2	2338.3	2.55

TABLE NO. 3.

SPECIFIC GRAVITIES OF AMMONIA SOLUTIONS.

Lunge and Wiernik.

Specific Gravity at 15° C.	Per cent NH₃.	Difference in Specific Gravity for 1° C.	Difference in Per cent for 0.001 Specific Gravity.	Specific Gravity at 15° C.	Per cent NH₃.	Difference in Specific Gravity for 1° C.	Difference in Per cent for 0.001 Specific Gravity.
0.980	4.80	0.00023		0.930	18.64	0.00042	0.305
0.978	5.30	0.00023	0.250	0.928	19.25	0.00043	0.305
0.976	5.80	0.00024	0.250	0.926	19.87	0.00044	0.310
0.974	6.30	0.00024	0.250	0.924	20.49	0.00045	0.310
0.972	6.80	0.00025	0.250	0.922	21.12	0.00046	0.315
0.970	7.31	0.00025	0.255	0.920	21.75	0.00047	0.315
0.968	7.82	0.00026	0.255	0.918	22.39	0.00048	0.320
0.966	8.33	0.00026	0.255	0.916	23.03	0.00049	0.320
0.964	8.84	0.00027	0.255	0.914	23.68	0.00050	0.325
0.962	9.35	0.00028	0.255	0.912	24.33	0.00051	0.325
0.960	9.91	0.00029	0.280	0.910	24.99	0.00052	0.330
0.958	10.47	0.00030	0.280	0.908	25.65	0.00053	0.330
0.956	11.03	0.00031	0.280	0.906	26.31	0.00054	0.330
0.954	11.60	0.00032	0.285	0.904	26.98	0.00055	0.335
0.952	12.17	0.00033	0.285	0.902	27.65	0.00056	0.335
0.950	12.74	0.00034	0.285	0.900	28.33	0.00057	0.340
0.948	13.31	0.00035	0.285	0.898	29.01	0.00058	0.340
0.946	13.88	0.00036	0.285	0.896	29.69	0.00059	0.340
0.944	14.46	0.00037	0.290	0.894	30.37	0.00060	0.340
0.942	15.04	0.00038	0.290	0.892	31.05	0.00060	0.340
0.940	15.63	0.00039	0.295	0.890	31.75	0.00061	0.350
0.938	16.22	0.00040	0.295	0.888	32.50	0.00062	0.375
0.936	16.82	0.00041	0.300	0.886	33.25	0.00063	0.375
0.934	17.42	0.00041	0.300	0.884	34.10	0.00064	0.425
0.932	18.03	0.00042	0.305	0.882	34.95	0.00065	0.425

CHAPTER XVI.

Part I.

AN AUTOMATIC STEAM WATER STILL.

AFTER submitting to considerable annoyance from several types of water stills, the author decided to try steam coils as a source of heat.

The boiling of water by this means is not a new idea, but after more than a year's trial, there was finally evolved a form of still, which has proven so satisfactory and the flow of the water has been so abundant that the details of the apparatus may be of assistance to someone else.

Two of these stills are in use in our laboratory operating but part of each day. The supply is ample for all analytical needs and for drinking water, which is also furnished to a large office force.

Cold water from the tap enters the condenser jacket, C, through the cock A. The condenser jacket is a cylindrical copper vessel eleven inches in diameter and fifteen inches high. The cooling water overflows at B to a sink not shown. A glass tube siphon S', S''', S''' dipping into the water slightly below the level of B carries hot water continually to the heating chamber D by way of the large copper feed funnel F', F''.

When the water in D has risen several inches the steam is turned into the worm coils of D at the valve V. These coils consist of two twelve-foot lengths of three-fourths inch bore copper pipe, brazed together and coiled around the inside walls of D. The steam from the boiling water rises into the dome and passes off through a block tin con-

densing pipe of five-eighths inch * inside diameter at T and travels through this pipe, which is coiled in a worm as shown in C.

The tin pipe passes through the tubular outlet O', O'' and delivers the distilled water on a filter paper supported by a six-inch ribbed glass funnel W. The filter papers are thirty cm. and are folded to fit the funnel. A piece of cheese-cloth is folded in the apex of the filter paper cone to prevent the weight of the water from breaking the paper. The filter paper catches any oily matter or other particles carried over with the steam.
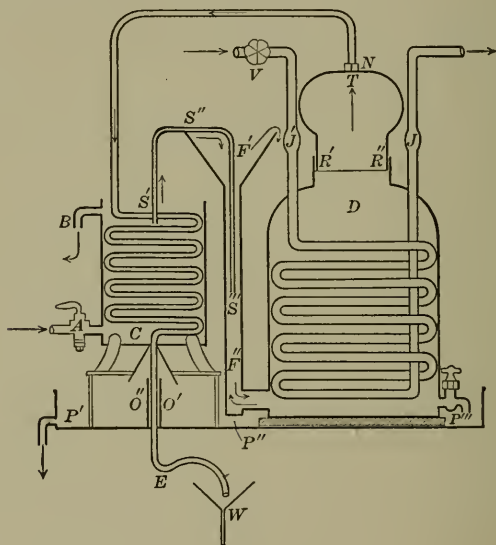
Fig. 1.

The distillate is delivered to the receiving funnel at the rate of one liter every 3 minutes when sufficient pressure is maintained in D to keep the copper funnel F', F'' filled nearly to overflowing with hot water.

* The larger the inside diameter of the tin worm the better to secure rapid condensation and a large output of water.

The water reservoir is a nine-gallon bottle, in the neck of which the funnel W rests. The bottle, which is not shown, is inclosed in a cupboard in which is an electric light to dispel darkness and roaches. This bottle rests in a copper pan, which is drained to the sewer. The tin pipe is bent into an elbow at E so that any condensation of moisture on damp days drips off at E instead of running down the pipe into W.

Steam pressure furnished from the mills is liable to continual variation. The amount of pressure may be nicely adjusted at V, but subsequent increase of pressure often causes the water to boil over at F and splash down into the copper pan P', P'', P''', which is drained at P'. The pan is five inches deep and large enough to contain the entire apparatus.

To clean the still the tin pipe is unscrewed at N, the dome head removed, and water is played on the interior of D with a hose, washing the sediment out through the cock at P'''.

The steam dome rests in the neck of D and is calked steam tight with cheese-cloth. The cloth is stretched in a diaphragm across R'', R', with enough excess of cloth for calking purposes.

The boiling of the water in F', F'' in no way prevents the action of the siphon S', S'', S'''. The heating coils of D are joined to ordinary steam pipes of the same diameter at J', J''.

This still could be made in any size to suit a greater or less production than that mentioned. A smaller size for a household or small laboratory, and in larger sizes for office buildings or for manufacturers needing a large supply of distilled water.

CHAPTER XVI.

PART. II.

CLAY COMBUSTION BOATS.

THE clay boats are made from Klingenberg clay. A typical analysis of it is given herewith:

	Per cent.
Protoxide of iron	2.67
Silica	52.48
Alumina	29.46
Ignition loss	14.18

Any plastic clay free from grit would answer just as well. The clay is ground to pass a thirty-mesh sieve; is thoroughly kneaded to a stiff dough with water. It is then rolled in a towel. By wetting the towel occasionally, the clay can be kept ready to use as long as desired.

The clay is rolled on a moist plaster-of-paris slab into a cigar shape and pressed into the plaster-of-paris mold with the thumbs. The excess clay is scraped off with a thin-edged piece of wood. The guide strip is then laid on the mold. It is the exact duplicate of the face of the mold, or *pmno* as shown in the plan. This strip, of course, has an opening in it coinciding exactly with *IcdJ*. The strip can be fastened on by a gum band at each end. The wooden tool T is plunged down through this slot, and, while being held perfectly vertical, it is slid along the wooden guide strip, scooping out the clay and shaping the interior of the boat. The tool slides along the strip on its surfaces at R and R'. The distance from c' to R and from R' to d' are equal and conform to the thickness of the guide strip. The distance $c'd'$ equals *cd*.

$c'V$ and $V'd'$ regulate the thickness of the walls of the boat. $Vf'V'$ forms the interior of the boat. The tool T is rounded on one side and is trimmed to a thin edge on the rounded side. The tools are kept in water when not in the operator's hand, to prevent the clay from sticking to

Plan of Mold
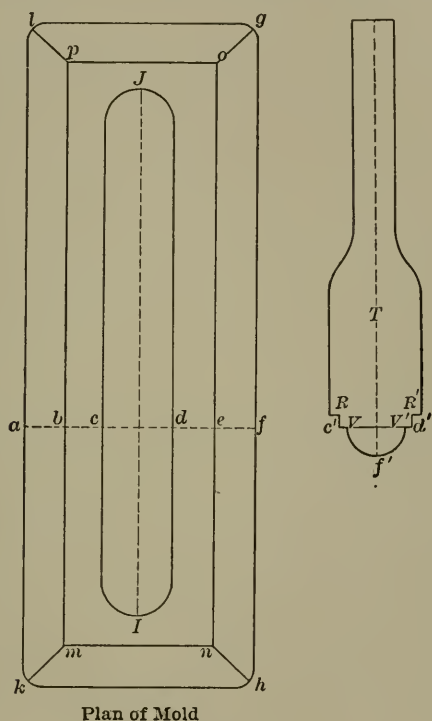
FIG. 2.

them. The interior of the mold has a flat bottom. The author prefers a boat of the following outside dimensions when burned: 15 mm. wide at top × 7 mm. wide at bottom × 9 mm. high × 131½ mm. long. The bowl of the mold should be about 6 per cent larger in all its dimensions to allow for shrinkage.

After the interior has been properly shaped, the guide strip is removed, the face of the mold scraped clean, and the mold put away in a warm place for the clay to dry. Slow drying for one or two days is the best. When the boats no longer seem damp to the touch, they are removed from the molds and dried for several hours in an air bath at a temperature of 120° C. They are then put in a muffle furnace, and the latter is lighted and the heat brought as quickly as convenient to a temperature of 850° C. to 900° (very bright red-heat) and kept at that temperature for from two to four hours. The heat is then turned off and the boats are ready for use. A boy can easily mold forty boats in three hours, and, after the molding is completed, the remaining operations require but a few moments' attention to make the transfers from the drying space to the air bath, and from the latter to the muffle furnace.

The boat should have walls and bottoms about $\frac{1}{16}$ inch thick. Boats made as described answer all of the purposes of porcelain boats, and, one can readily see, are extremely cheap. The writer first experimented with a view to making his own boats, more than a year ago, and now uses them for all combustion work. A layer of ignited silica sand is a good protection for these boats for carbon combustions unless the use of red lead is necessary, and, indeed, at all times except for the combustion of materials that leave a non-fluxing ash such as plumbago or coals.

It is convenient to have the dimension Kh, 62 mm.; hg, 177 mm., and the total thickness of the mold 25 mm.

When the boats have been burned, two or three from each batch should be placed in the combustion furnace and a blank analysis made. If the weighing apparatus shows a gain of more than 0.0002 gram, it is an indication of imperfect burning of the boats. They should be reburned until free from all carbonaceous matter.

The author wishes to acknowledge the assistance and advice rendered him by the superintendent of the plumbago crucible factory of this works, Mr. Bayard Guthrie, in working out the method of making a cheap substitute for porcelain combustion boats.

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